

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 DCI-CH₃OH¹

BY A. G. GASSMANN,² C. J. HOCHANDEL AND R. J. HARTMAN³

Following the procedure of Hartman and Borders⁴ 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 equation⁵ 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 Borders⁴ and Hartman and Gassmann⁶ 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	DCI	10 ⁴ k	HCl ⁴
<i>o</i> -Toluic	6.61		6.41
<i>m</i> -Nitrobenzoic	7.29		7.28
<i>p</i> -Nitrobenzoic	8.04		8.67
<i>p</i> -Chlorobenzoic	10.5		11.4
<i>m</i> -Chlorobenzoic	11.6		12.4
<i>m</i> -Iodobenzoic	13.6		13.7
<i>p</i> -Toluic	18.5		19.7
Benzoic	19.1		19.2
<i>m</i> -Toluic	21.8		21.7

This identity was of course to be expected in view of the known rapid exchange reaction in the system, DCI-CH₃OH. It was found that the rate at which 0.1000 *N* and 0.0200 *N* DCI reacts with methanol at 25, 40, 50, and 60° was ap-

(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).

proximately the same as that previously reported for hydrogen chloride and methanol.⁷

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

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INDIANA UNIVERSITY
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Reactions of Nickel(II), Nickel(II,III), and Iron(III) Oxides in Liquid Ammonia¹

BY ROLAND B. HOLT AND GEORGE W. WATT

Subsequent to the work of Moore and Watt² 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*.^{4,5} Calcd. for Ni₂O₃: Ni, 73.35. Found: Ni, 73.85. *Iron(III) oxide*. Calcd. for Fe₂O₃: 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(NH₃)₆(NO₃)₂: Ni, 20.5; NH₃, 35.7. Found: Ni, 20.1; NH₃, 35.5.

The analogous reaction with ammonium chloride solu-

(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 (1918).