

tions, 4-phenylphenyl chloroacetate gave rise to the analogous bromination product.<sup>2</sup>

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### Evidence of Deuterium Exchange in the System DCI-CH<sub>3</sub>OH<sup>1</sup>

BY A. G. GASSMANN,<sup>2</sup> C. J. HOCHANDEL AND R. J. HARTMAN<sup>3</sup>

Following the procedure of Hartman and Borders<sup>4</sup> 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<sup>5</sup> 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<sup>4</sup> and Hartman and Gassmann<sup>6</sup> 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 <sup>4</sup> k	HCl <sup>4,6</sup>
<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-CH<sub>3</sub>OH. 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.

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(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.<sup>7</sup>

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

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### Reactions of Nickel(II), Nickel(II,III), and Iron(III) Oxides in Liquid Ammonia<sup>1</sup>

BY ROLAND B. HOLT AND GEORGE W. WATT

Subsequent to the work of Moore and Watt<sup>2</sup> 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,<sup>2</sup> only the conclusions arising from these latter experiments are included here.<sup>3</sup>

#### 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*.<sup>4,5</sup> Calcd. for Ni<sub>2</sub>O<sub>3</sub>: Ni, 73.35. Found: Ni, 73.85. *Iron(III) oxide*. Calcd. for Fe<sub>2</sub>O<sub>3</sub>: 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.<sup>6</sup>

*Anal.* Calcd. for Ni(NH<sub>3</sub>)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>: Ni, 20.5; NH<sub>3</sub>, 35.7. Found: Ni, 20.1; NH<sub>3</sub>, 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).

tions differed only in that lavender crystals of nickel(II) chloride 6-ammonate<sup>7</sup> were obtained.

*Anal.* Calcd. for  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ : Ni, 25.3;  $\text{NH}_3$ , 44.1; Cl, 30.6. Found: Ni, 25.6;  $\text{NH}_3$ , 44.2; Cl, 30.4.

**Reactions with Potassium Amide.**—Nickel(II) oxide was recovered unchanged after treatment with a liquid ammonia solution containing an excess of potassium amide for seventy-two hours at 25 or 100°. By similar treatment, nickel(II,III) oxide was converted to an intractable mixture of insoluble products. Essentially the same conversion resulted from treatment of this oxide with liquid ammonia solutions of potassium at 25°. At either 25 or 100°, iron(III) oxide reacted with liquid ammonia solutions of potassium amide to form mixtures of iron(II) oxide and elemental iron in relative quantities dependent upon the quantity of potassium employed.

**Reduction by Liquid Ammonia Solutions of Potassium.**—At 0°, nickel(II) oxide was reduced to elemental nickel by liquid ammonia solutions of potassium to an extent dependent upon the concentration of potassium used. With 2, 4, 8 and 12 equivalents of potassium, reduction occurred to the extent of 0.3, 0.5, 1.4, and 4.3%, respectively. The weights of potassium amide formed concurrently<sup>8</sup> (as shown by analysis), agreed closely with corresponding values calculated on the basis of (a) the volumes of hydrogen liberated, and (b) the quantities of elemental nickel produced.

The catalytic activity of nickel(II,III) and iron(III) oxides (or that of very small quantities of their reduction products) toward the conversion of potassium to potassium amide was so pronounced that appreciable reduction of these oxides (by ammonia solutions of potassium) could not be accomplished. The decreasing order of catalytic activity is  $\text{Fe}_2\text{O}_3 > \text{Ni}_2\text{O}_3 > \text{NiO}$ .

(7) Rose, *Pogg. Ann.*, **20**, 155 (1830).

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## The Nitration of Methyl $\alpha$ -Naphthoate and Related Compounds<sup>1</sup>

BY C. F. KOELSCH AND DONALD O. HOFFMAN

Because the nitration of methyl benzoate takes place so much more smoothly than does that of benzoic acid,<sup>2</sup> it was hoped that the nitration of methyl  $\alpha$ -naphthoate might yield methyl 3,8-dinitronaphthoate among the dinitration products. It has been found, however, that the main product of this reaction is methyl 4,5-dinitronaphthoate, a substance which is also formed when methyl 5-nitronaphthoate is nitrated. The nitration of methyl 8-nitronaphthoate yields a dinitro ester which appears to be methyl 4,8-dinitronaphthoate. In none of the naphthoic

ester nitrations does the reaction take place smoothly; oily by-products are formed, and unless the temperature is kept close to 0°, gas is evolved and much hydrolysis occurs. This is not similar to the behavior of methyl benzoate, where neither hydrolysis nor by-product formation is important at 15° or higher.

In the nitration of  $\alpha$ -naphthoic acid there is formed a small amount of an acid not previously reported, which is probably 6,8-dinitronaphthoic acid. A stable molecular compound of naphthoic acid with 5-nitronaphthoic acid has also been isolated.

### Experimental

**Methyl  $\alpha$ -Naphthoate.**—The ester (b. p. 167–169° at 20 mm.) was obtained in 89% yield by passing methanol vapor (600 g.) at 85–100° during ninety minutes through 113 g. of  $\alpha$ -naphthoic acid mixed with 10 ml. of concd. sulfuric acid and 300 ml. of methanol.<sup>3</sup>

To a solution of 10 g. of methyl  $\alpha$ -naphthoate in 33 ml. of concd. sulfuric acid, a solution of 10 ml. of nitric acid (d. 1.2, 3 eq.) in 10 ml. of concd. sulfuric acid was slowly added at 0–10°. The mixture became red-black almost at once, and much heat was evolved during the addition of the first two-thirds of the nitric acid. After the addition was completed, the mixture was allowed to stand at 0° for ten minutes and then poured on ice. The sticky product was washed with dilute sodium carbonate (which removed 5- and 8-nitro- and a small amount of 4,5-dinitro-naphthoic acids) and then with ether-ligroin. The insoluble material (4.0 g., m. p. 140–185°) was crystallized from toluene and then from acetic acid, giving 2.12 g. of methyl 4,5-dinitronaphthoate which formed nearly colorless needles that melted at 194–195°.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_6$ : C, 52.2; H, 2.9. Found: C, 52.2; H, 2.9.

The ester was identified by hydrolysis (acetic acid, water and sulfuric acid); the resulting 4,5-dinitronaphthoic acid melted at 266–267° (reported<sup>4</sup> 265°), and on boiling for fifteen minutes in quinoline containing a little copper acetate yielded 1,8-dinitronaphthalene, m. p. 170–172°.

Oily material and about 3 g. of crystalline material were present in the ether-ligroin washings of the crude nitration product, but no pure substance could be isolated from these.

Duplicate experiments and others in which up to five equivalents of nitric acid in sulfuric acid was used gave results quite similar to those described. However, when less nitric acid was used, less dinitronaphthoic ester and more 5- and 8-nitronaphthoic acids were obtained. Nitration in the absence of sulfuric acid, using fuming nitric acid, gave mainly a mixture of methyl 5- and 8-nitronaphthoates, little hydrolysis or dinitration taking place.

**Methyl 5-Nitronaphthoate.**—The ester, prepared in 70% yield by boiling 5-nitronaphthoic acid (5.1 g.) with methanol (50 ml.) and sulfuric acid (1 ml.) for five hours,

(1) From the M. S. thesis of D. O. Hoffman, March, 1941.

(2) Kamm and Segur, "Organic Syntheses," Coll. Vol. 1, 1932, p. 364.

(3) Cf. Corson, Adams and Scott, "Organic Syntheses," **10**, 48 (1930).

(4) Ekstrand, *J. prakt. Chem.*, **38**, 256 (1888).