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[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

ON THE OXYGEN ETHERS OF UREA.

By W. M. Bruce.

Received February 6, 1904.

(Continued from p. 436.)

II. CONDENSATIONS OF THE ISOUREAS.

Sym. O-Methyl Diphenyldiureidoisourea,

$C_6H_5NHCONHC(OCH_3):NCONHC_6H_5$.

—Methyl phenylisobiuret, 0.6 gram, prepared according to the method of Stieglitz and McKee, was treated with 0.3 gram phenylisocyanate, the material being kept cold. The product soon became semi-fluid and after standing over night the contents of the tube had become solid. This solid was washed a great many times with ether and then melted constant at 153°. It gave: C, 61.60; H, 5.46. Calculated: C, 61.47; H, 5.18.

Some of the above compound was dissolved in absolute ether and treated with a little dry hydrogen chloride. The precipitate was filtered off, washed with absolute ether and dried as usual for one and a half hours. The salt melted at 122°, giving off methyl chloride. A chlorine determination gave results agreeing best with a sesquichloride. There was found 14.81 per cent. Cl. Calculated for $(C_{16}H_{16}O_3N_4)_2.3HCl$, 14.48 per cent.

Carbonyl Diphenyldiurea, $(C_6H_5NHCONH)_2CO$.—Some of the diureïd was placed in a sample tube and treated with dry hydrogen chloride at 60°. Methyl chloride was evolved and a colorless solid was left which melted sharply at 211°. As the quantity was small, the substance was placed in a desiccator for a day or two and then analyzed without further purification. It gave: C, 60.50; H, 5.20. Calculated: C, 60.34; H, 4.74.

O-Methyl Carbethoxyisourea, $C_2H_5OCONC(OCH_3)NH_2$.—Methyl isourea hydrochloride, 2 grams, was treated at 0°, in ethereal solution with potassium hydroxide (2.2 grams dissolved in 1.5 cc. water) and ethyl chlorformate (1.9 gram). The dried ether extracts left a colorless mobile oil, which, when it was cooled in a freezing-mixture and persistently scratched, solidified completely. The substance was purified by precipitation from ether solution by petroleum ether. The melting-point is 5°. The analysis gave: C, 41.15; H, 7.21. Calculated: C, 41.05; H, 6.91.

O-Methyl Carbethoxyisourea Hydrochloride,
$C_2H_5OCONC(OCH_3)NH_2.HCl$.
—Some methyl carbethoxyisourea was dissolved in absolute ether and dry hydrogen chloride passed into the solution. The precipitate was filtered off, washed and dried as usual and analyzed (I, II and III) after an interval of half an hour and again (IV) after a week. There was found, I, 17.72, II, 18.02, III, 19.16, and IV, 15.15 per cent. Cl. Calculated, 19.40 per cent.

These results show a gradual decomposition with loss of chlorine. The decomposition occurs as follows:

$$C_2H_5OCONC(OCH_3)NH_2.HCl \rightarrow CH_3Cl + C_2H_5OCONHCONH_2.$$

This was confirmed by the following: Some methyl carbethoxyisourea was treated with dry hydrogen chloride; at the ordinary temperature, methyl chloride was evolved. The solid residue was washed with water and dried; it then melted at 191° and was recognized as allophanic ester.

Some of the hydrochloride, when heated, evolved methyl chloride in quantity at 90°.

All attempts to introduce a second carbethoxyl group left the body unchanged.

O-Methyl Thiophenylureidoisourea,
$(C_6H_5NHCSN:)C(OCH_3)NH_2$.
—Methyl isourea, 0.2 gram, was mixed with 0.5 gram phenyl mustard oil; heat was evolved and the product soon solidified when it was cooled. The substance was purified by several recrystallizations from hot benzene. Obtained thus, the compound consists of diamond-shaped plates, insoluble in water and ether but easily soluble in chloroform. The melting-point is 131°.

The compound can also be obtained much more conveniently by warming the isourea hydrochloride with phenyl mustard oil and potassium hydroxide in the presence of a little water. The yield, however, is much less by this method.

The substance is somewhat unstable. When kept in a desiccator several days it melted at 121°-126° and on analysis (I) gave a low nitrogen content. Another sample (II) was analyzed after remaining in a vacuum only two hours. The results were 19.04 and 19.92 per cent. N. Calculated, 20.13 per cent.

Methyl phenylisothiobiuret was dissolved in chloroform and dry hydrogen chloride added. The white crystalline precipitate was dried and when heated to 115° melted with evolution of methyl chloride.

Methyl phenylisothiobiuret, when treated with dry hydrogen chloride and heated to 75°-90°, gave off methyl chloride. The solid phenylthiobiuret remaining in the tube was recrystallized from absolute alcohol and obtained in the form of very fine needles, which melted at 171° with decomposition, a gas being evolved having an odor similar to that of mercaptan.

While methyl isourea condenses with 2 molecules of phenylisocyanate, it reacts only with 1 molecule of phenyl mustard oil.

O-Methyl Isobiuret, $H_2NCON:C(OCH_3)NH_2$.—One gram methyl isourea hydrochloride was dissolved in 4 cc. water and added to a solution of 0.08 gram potassium isocyanate in 4 cc. water and the mixture allowed to evaporate to dryness in a warm place. The residue was extracted repeatedly with boiling benzene. The benzene solution was evaporated and 0.2 gram of a solid was obtained which melted at 110°. Some of this solid, when treated with dry hydrogen chloride, began to evolve methyl chloride at the room temperature and left a product which, thoroughly washed with water and dried, melted at 190°—the melting-point of biuret. It also gave the biuret reaction with copper sulphate and sodium hydroxide. Methyl isobiuret, when purified by recrystallization from hot benzene, melted at 118°.

The analysis gave: C, 30.98; H, 6.30. Calculated: C, 30.72; H, 6.03.

Benzylidene Dimethyldiïsourea,

$$C_6H_5CH:(NHC(OCH_3):NH)_2.$$

—Methyl isourea, 0.72 gram, was added to 1 gram (a mol.) benzaldehyde. Nearly all the methyl isourea dissolved in a few minutes without heat evolution. After standing for about two days, the substance was almost completely solid. This solid, insoluble in ether, acetone and chloroform but soluble in methyl alcohol, was washed many times with absolute ether. It then melted constant at 137°. The ether washings were treated with dry hydrogen chloride and allowed to stand and a small amount of a crystalline substance separated which melted at 235°. Tribenzotetraureïd melts at 240°.

The substance melting at 137° was analyzed and gave: C, 55.33; H, 6.81. Calculated: C, 55.85; H, 6.84.

It is evident from the above that 2 molecules of methyl isourea reacted with one of the benzaldehyde as follows:

$$2H_2NC(OCH_3):NH + C_6H_5CHO \rightarrow C_6H_5CH:[NHC(OCH_3):NH]_2 + H_2O.$$

Small quantities of a tribenzylidene tetraisourea were formed at the same time.

Some of the diisourea when treated with dry hydrogen chloride evolved methyl chloride at the room temperature. The residue, benzylidene diureïd, was washed with ether and acetone and began to decompose when heated to 195°-200° and melted at 210°, giving off a little gas. Schiff[1] gives the melting-point of his benzodiureïd as 195° and adds that heated higher it decomposed. Richter gives the melting-point 200°.

The following experiment was made in the attempt to obtain the hydrochloride. The isodiureïd was dissolved in absolute methyl alcohol and dry hydrogen chloride slowly passed into the cold solution. A precipitate, obtained by the addition of ether, was filtered off, washed and dried as usual for two hours.

It then melted at 85°, giving off methyl chloride. It gave, by

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[1] *Ann. Chem.* (Liebig), **151**, 192 (1869).

titration, 19.37 per cent. Cl. Calculated for $C_{11}H_{16}O_2N_4.2HCl$, 22.91 per cent.

Benzylidene Diethyldiisourea,

$$C_6H_5CH:[NHC(OC_2H_5):NH]_2.$$

—Ethyl isourea, 0.7 gram, dissolved in a little absolute ether, was mixed with 0.84 gram (1 mol.) redistilled benzaldehyde. After standing two weeks, a white crystalline mass was obtained which was thoroughly washed many times with absolute ether and finally with a little acetone. The substance then melted at 154° and was insoluble in water, ether and alkalies and nearly insoluble in benzene, but soluble in chloroform, acetone and in dilute acids. No definite crystalline form could be observed under the microscope.

The analysis gave: C, 59.19; H, 7.51. Calculated: C, 59.01; H, 7.64.

An impure hydrochloride of the isodiureïd was obtained by treating a chloroform solution of the ureïd with dry hydrogen chloride. When heated, this salt melted and gave off ethyl chloride at 90°. The chloride was allowed to stand in the air in a warm place for several hours. The melting-point was then found to be 195°—the melting-point of benzodiureïd. Evidently complete decomposition had occurred.

Some ethyl isourea and benzaldehyde were mixed in equimolecular quantities and the mixture allowed to stand for several months. The product was then washed with ether and treated with dry hydrogen chloride. Ethyl chloride was evolved and a solid residue remained which, when purified, melted at 240° with decomposition. This is the melting-point tribenzylidene tetraureïd. Evidently the substance formed by the long-continued action of benzaldehyde was a much higher condensation product than that first obtained. This substance, as is shown by its decomposition product, tribenzylidene tetraureïd, was tribenzylidene tetrethyl isotetraureïd.

By condensation of isourea ethers with β-keto-acid esters the oxygen ethers of μ-oxypyrimidines were easily obtained. Their ready formation by this method promises to be serviceable in synthetic work in the uric acid series.[1]

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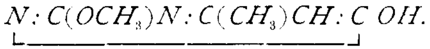
[1] Mr. R. W. Noble is carrying out work along this line in this laboratory.—J. S.

μ-Methoxy-α-methyl-γ-oxypyrimidine,

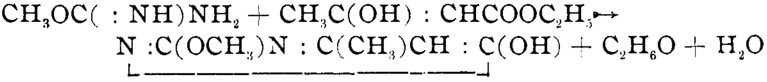


$$N:C(OCH_3)N:C(CH_3)CH:C\,OH.$$

—A mixture of 0.5 gram methyl isourea and 0.8 gram (1 mol.) acetoacetic ether formed a light yellow oil which, after standing a day or two or upon being warmed on the water-bath to 50° for a few minutes, almost completely solidified. The product was thoroughly washed with ether and crystallized from boiling alcohol in feathery masses of needles which melted constantly at 207° after several recrystallizations. The yield was about 90 per cent. of the theoretical. The pyrimidine is insoluble in the ordinary organic solvents in the cold, readily soluble in boiling benzene or alcohol, as well as in dilute acids or alkalies.

The analysis gave: C, 51.26; H, 5.93. Calculated: C, 51.37; H, 5.76.

The reaction between methyl isourea and acetoacetic ether is analogous to that between the amidines and acetoacetic ether,[1] and may be given as follows:



$$CH_3OC(:NH)NH_2 + CH_3C(OH):CHCOOC_2H_5 \rightarrow$$
$$N:C(OCH_3)N:C(CH_3)CH:C(OH) + C_2H_6O + H_2O$$

The splitting off of both alcohol and water seems to be simultaneous, as no indications of any intermediate products were ever found.

A little of the oxypyrimidine was dissolved in the minimum amount of ethyl alcohol and treated with a slight excess of hydrochlorplatinic acid, also in concentrated solution. Absolute ether was now added and an oil was precipitated, which soon crystallized in the form of yellow spindle-shaped needles. The crystals were dried for half an hour, and then gave 28.33 per cent. Pt. Calculated for $(C_6H_8O_2N_2)_2H_2PtCl_6$, 28.24 per cent.

A small amount of the oxypyrimidine was dissolved in dry benzene and treated with dry hydrogen chloride. The precipitate was dried *in vacuo* over solid potassium hydroxide for half an hour.

Some of the hydrochloride evolved methyl chloride when heated to 90°-100°. The solid residue began to decompose when heated to 270°, proving it to be methyl uracil—formed according to

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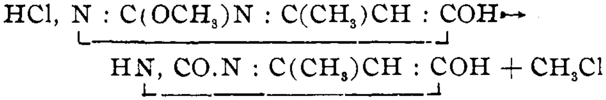
[1] Pinner: "Imidoäther," p. 216.

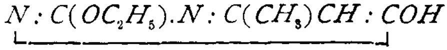


$$HCl, N : C(OCH_3)N : C(CH_3)CH : COH \rightarrow HN, CO.N : C(CH_3)CH : COH + CH_3Cl$$

By titration there was found 20.03 per cent. Cl. Calculated, 20.06 per cent.

The silver salt was obtained from 0.2 gram of the oxypyrimidine dissolved in absolute methyl alcohol, by the addition of a methyl alcohol solution of sodium methylate (prepared from the calculated amount of sodium) and then of the equivalent amount of silver nitrate in a mixture of methyl alcohol and water (1 : 1). A very thick gelatinous precipitate formed which it was impossible to wash even with the pump. It was placed on a clay plate *in vacuo* for several days until it was perfectly dry, then finely powdered and washed repeatedly with water, methyl alcohol and ether, and dried as before. It thus gave 43.36 per cent. Ag. Calculated for $C_6H_7O_2N_2Ag$, 43.65 per cent.

μ-Ethoxy-α-methyl-γ-oxypyrimidine,



$$N : C(OC_2H_5).N : C(CH_3)CH : COH$$

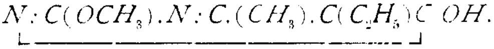
—Ethyl isourea, 2 grams, was mixed with 3 grams (1 mol.) acetoacetic ether. The mixture, warmed at 60° for one hour, almost completely solidified. This solid, when washed with absolute ether and recrystallized from boiling absolute alcohol, was obtained in the form of fine shining needles, which melted at 206°. These gave: C, 54.43; H, 6.73. Calculated: C, 54.48; H, 6.55.

The chlorplatinate was prepared by the method described above for the corresponding methyl derivative. The crystals were yellow needles, which gave 26.95 per cent. Pt. Calculated, 27.14 per cent.

A small amount of the oxypyrimidine in concentrated benzene solution was treated with a little dry hydrogen chloride. The precipitate was washed with dry benzene and dried for forty minutes (I) and eighteen hours (II), respectively. By titration these gave, 17.49 and 17.78 per cent. Cl. Calculated for $C_7H_{10}O_2N_2HCl$, 18.59 per cent.

Some of the oxypyrimidine was heated in a stream of dry hydrogen chloride and evolved ethyl chloride at 90°-130°. The solid residue decomposed when heated to 270°. It was methyl uracil.

μ-Methoxy-α-methyl-β-ethyl-γ-oxypyrimidine,



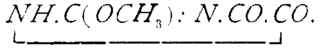
$$N:C(OCH_3).N:C.(CH_3).C(C_2H_5)C\cdot OH.$$

—Methyl isourea, 0.6 gram, was mixed with 1.2 grams (1 mol.) ethyl acetoacetic ether. The mixture formed a clear oil which on standing over night became filled with four-sided needles in masses from a common center. The crystals were washed with absolute ether and after several recrystallizations from hot absolute alcohol melted constant at 210°.

The compound is easily soluble in acid or alkali. The analysis gave: C, 56.94; H, 7.43. Calculated: C, 57.07; H, 7.20.

An attempt was made to prepare the hydrochloride from the oxypyrimidine in benzene or chloroform solution and dry hydrogen chloride, but the product was always mucilaginous and not easily purified. However, the salt was easily obtained from a solution of 0.3 gram oxypyrimidine in the calculated amount of hexanormal hydrochloric acid, by evaporation *in vacuo*. After standing *in vacuo* nearly a day the dry salt was analyzed, and gave 17.12 per cent. Cl. Calculated for $C_8H_{13}O_2N_2Cl$, 17.31 per cent.

O-Methyl Oxalylisourea, (μ-Methyl Parabanic Acid),



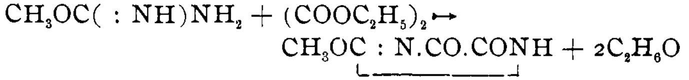
$$NH.C(OCH_3):N.CO.CO.$$

—Methyl isourea, 0.4 gram, was mixed with a slight excess (1 gram) oxalic ester. In a few minutes the whole mass apparently became solid. After standing for several days, the compound was washed repeatedly with ether, benzene and petroleum ether and then recrystallized from absolute alcohol. It was obtained in the form of three-sided prisms, which melt at 137.5°. The crystals are insoluble in ordinary organic solvents, but easily soluble in water, alkali and boiling alcohol.

The chlorplatinate of this substance was prepared and analyzed as follows: A small amount of the compound was dissolved in absolute alcohol and about the calculated quantity of hydrochlorplatinic acid, also in absolute alcohol, was added. Upon the addition of dry benzene, a bright yellow solid separated.

This gave 29.60 per cent. Pt. Calculated for $C_8H_{10}O_6N_4PtCl_6$, 29.71 per cent.

The reaction by which methyl oxalylisourea is formed may be given as follows:



$$\mathrm{CH_3OC(:NH)NH_2 + (COOC_2H_5)_2 \mapsto}$$
$$\mathrm{\underbrace{CH_3OC : N.CO.CONH}_{} + 2C_2H_6O}$$

Some of the compound, when treated with a little dilute hydrochloric acid, dissolved completely at first and then almost immediately deposited a solid. This solid, dried *in vacuo*, was gently heated, dissolved in alcohol and reprecipitated by petroleum ether. The substance thus obtained began to decompose when heated to 190°. It was undoubtedly oxalylurea.

III. THE AFFINITY CONSTANTS OF ISOUREAS.

For an isourea which is ionized according to

$$\mathrm{HN:C(OR)NH_2,\ H_2O \rightleftarrows HN:C(OR)\overset{+}{N}H_3 + \overset{-}{OH}},$$

and which does not belong to the class of strongest bases,[1] such as the alkalies, we would have the affinity constant, K, expressed in the following equation:

$$C_{OH} \times C_P = K \times C_n. \qquad (1)$$

C_{OH} and C_P are the concentrations of the hydroxyl ions and the positive base ions in terms of gram ions per *liter* and C_n is the concentration of the non-ionized amine.

The affinity constants of the most important representatives of the typical classes of isoureas, $\mathrm{H_2NC(OR):NH}$, and (alphyl) $\mathrm{HNC(OR):NH}$, were determined by the conductivity method as developed by Ostwald,[2] and van't Hoff[3] and as applied especially by Bredig[4] to the measurement of the affinity constants of bases. The proportion (α) of the base ionized in a given solution was ascertained from the molecular conductivity of the solution from the relation

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}. \qquad (2)$$

n which Λ_v expresses the molecular conductivity of the base vhen 1 gram-molecule is dissolved in *v cc.* water, and Λ_∞ is the xtreme molecular conductivity.

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[1] For the strongest bases, as is well known, equation (1) does not hold good. Vide udolphi: *Ztschr. phys. Chem.*, **17**, 385; Van't Hoff: *Ibid.*, 18, 301; Kohlrausch: *Ibid.*, **18**, 51. The isomers, as will be shown below, give good constants according to (1) and be- ng, therefore, to the so-called class of "half electrolytes." (Van't Hoff: "Theoretical nd Physical Chemistry," I, p. 117.)

[2] *Ztschr. phys. Chem.*, **2**, 36, 270 (1888).

[3] *Ibid.*, **2**, 781 (1888).

[4] *Ibid.*, 13, 289 (1893).

Then if we express by Λ the number of liters[1] containing 1 gram-molecule of the amine, equation (1) resolves itself into

$$\frac{\alpha^2}{1-\alpha} = KV. \qquad (3)^2$$

The molecular conductivities Λ_v of the bases were determined by conductivity measurements made with solutions of the free bases. The Kohlrausch apparatus was used and the measurements made at a temperature of 25° (± 0.01°). The molecular conductivities of the bases in the extreme dilution, Λ_∞, were ascertained in the usual way by a determination of the extreme molecular conductivity, Λ'_∞, of the hydrochlorides of the bases—and by calculation of Λ_∞ according to the well-known equation,

$$\Lambda_\infty = \Lambda'_\infty - l_{\infty \mathrm{Cl}} + l_{\infty \mathrm{OH}} \qquad (4)$$

in which Λ_∞ and Λ'_∞ are the extreme molecular conductivities of the free bases and the hydrochlorides respectively and $l_{\infty \mathrm{OH}}$ and $l_{\infty \mathrm{Cl}}$ represent the extreme mobility of the hydroxyl and the chlorine ions. $l_{\infty \mathrm{OH}}$ was taken as 195.8,[3] $l_{\infty \mathrm{Cl}}$ as 75.9,[4] both in reciprocal ohms, for 25°. By combining (2), (3) and (4) the constants, K, were calculated on the basis of the experimental determinations made. The results obtained with the various bases follow:

Methyl Isourea, $HN:C(OCH_3)NH_2$.—Methyl isourea chloride, prepared according to the method of Stieglitz and McKee,[5] and recrystallized twice from boiling absolute methyl alcohol, washed with absolute ether and placed *in vacuo* over solid potassium hydroxide and concentrated sulphuric acid for three days. A solution of some of this salt in water reacted neutral to sensitive litmus paper. An analysis gave 32.22 per cent. Cl. Calculated for $C_2H_6ON_2.HCl$, 32.04.

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[1] The conductivity measurements are given in this paper in reciprocal ohms, and all the units used in the measurements are those given in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," the unit of concentration being the gram-molecule (or equivalent) in 1 cc. The affinity constants, however, are given, in accordance with the more general usage, in terms of the unit of concentration of 1 gram-molecule *per liter*.

[2] Ostwald: *Ztschr. phys. Chem.*, **2**, 278 (1889).

[3] Kohlrausch (*Loc. cit.*, p. 200) gives for l_∞ OH at 18° the value 174 in reciprocal ohms. Its value at 25° was calculated with the aid of the temperature coefficient (α) for hydroxyl ions as determined by Loeb and Nernst (*Ztschr. phys. Chem.*, **2**, 963). $\alpha = 0.0159$ and $l_{18} = l_{25}[1 + \alpha(t-25)]$.

[4] Kohlrausch (*Loc. cit.*) gives for the extreme mobility of chlorine ions at 18° the value 65.9. The temperature coefficient for these ions is 0.022 of the value found at 18° (Arrhenius: "Electrochemistry," p. 142).

[5] *Loc. cit.*

The conductivity measurements with this salt are given in Table I, in which v is the volume in liters, containing a gram-molecule of the salt, Λ_v the molecular conductivity at 25° in reciprocal ohms, at the concentration in question. Λ'_∞, the extreme molecular conductivity of the salt, is found according to Ostwald's[1] and Bredig's[2] empirical law from each molecular conductivity, Λ_v, by adding values,[3] d_v, which are characteristic for the differences $\Lambda_\infty - \Lambda_v$, and which are approximately constant for salts in general.

TABLE I.

v.	Λv.		Λ'_∞.	
	I.	II.	I.	II.
32	104.06	104.04	119.1	119.0
64	107.97	107.97	119.7	119.7
128	111.30	110.98	119.9	119.6
256	113.15	113.05	119.55	119.7
512	115.87	115.51	120.2	119.8
1024	[120.12]	[118.17]	[123.3]	[121.4]
	Means (excluding $v = 1024$):		119.7	119.6

In taking the mean value for Λ'_∞, the value found when $v = 1024$, was excluded because of the obvious fact that at that dilution some irregularity manifests itself. The irregularity is either due to a slight hydrolysis or, much more likely, to the fact that at that dilution methyl isourea begins to act perceptibly as a diacid base.[4]

The agreement between the values for Λ'_∞ in each series and between the means for each series is very satisfactory. This fact shows that, except possibly in very high dilutions (when $v = 1024$) and probably not even then, there is no hydrolysis of the salt of any moment. Even the most dilute solutions were perfectly neutral to sensitive litmus paper and litmus solution.

Since $l_{\infty Cl} = 75.9$ at 25° we have $l_{\infty P} = 119.7 - 75.9 = 43.8$.

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[1] "Lehrbuch d. Allgem. Chemie," Vol. II, 693.

[2] *Ztschr. phys. Chem.*, **13**, 198.

[3] Bredig's values for dv were used, multiplied by the factor 1.066 to convert the reciprocal Siemens' units into reciprocal ohms (see Kohlrausch: *Loc. cit.*, p. 144, for the use of the factor 1.066 in place of 1.063, the international factor).

[4] Vide, Bredig: *Loc. cit.*, p. 122. For the case in question, the correctness of this latter view is demonstrated by the fact that the weaker bases of the series, the phenylisoureas, do not show any anomaly; their salts would be much more likely to suffer hydrolysis than the salts of the unsubstituted isoureas, but they would be much less likely to behave as diacid bases. Their normal behavior is good evidence, therefore, that the irregularity in the case of methyl and ethyl isourea when v is 1024 is due to the partial ionization of the latter as diacid bases.

That is, the extreme mobility of the positive ion of methyl isourea is 43.8.

The molecular conductivity of the free base in extreme dilution, Λ_∞, is found from equation (4).

$$\Lambda_\infty = l_{\infty \mathrm{P}} + l_{\infty \mathrm{OH}} = 43.8 + 195.8 = 239.6.$$

A sample of the free base was prepared according to the method of Stieglitz and McKee,[1] and dried next to solid potassium hydroxide for several hours. Its purity was ascertained by titration against tenth-normal hydrochloric acid (with methyl orange as indicator).[2]

0.0939 gram required 12.68 cc. tenth-normal HCl. Calculated, 12.66 cc.

The conductivity measurements for the free base at 25° are given in Table II, in which v and Λ_v have the same meanings as in Table I. In the third column the values for α are given as calculated according to equation (2), and in the last column the values for the affinity constant, K, are given as determined from equation (3).

TABLE II.

v.	Λv.		100α.		10^5K.	
	I.	II.	I.	II.	I.	II.
32	10.61	10.57	4.43	4.42	6.4	6.4
64	14.60	14.59	6.10	6.10	6.4	6.2
128	20.30	20.22	8.48	8.45	6.1	6.1
256	27.73	27.57	11.55	11.52	5.9	5.9
512	37.93	37.02	15.85	15.47	5.8	5.5
1024	51.74	49.35	21.62	20.62	5.9	5.2
				Means :	6.08	5.90

For comparison, the affinity constant of urea was calculated from the data given by Walker[3] on the hydrolysis of solutions of urea hydrochloride containing varying proportions of the acid and base. The constant, K, was derived according to Walker's formula

$$\frac{\text{Salt}}{\text{Acid} \times \text{Base}} = k$$

in which salt, acid and base represent the concentrations of the substances in gram-molecules per liter. The average constant was found to be 1.28 (± 0.06). This constant, according to

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[1] *Loc. cit.*

[2] Stieglitz and McKee : *Loc. cit.*

[3] *Ztschr. phys. Chem.*, **4**, 326 (1891) and *Ber. d. chem. Ges.*, **34**, 4117 (1901).

Arrhenius[1] is the constant ratio between the affinity constant of the base and the dissociation constant of water which is 1.2×10^{-14}. We find thus the affinity constant[2] of urea to be $1.28 \times 1.2 \times 10^{-14}$ or 1.54×10^{-14}. Urea is then but little stronger as a base than water—namely, about sixty times as strong.[3] The simplest isourea, methyl isourea, whose affinity constant, as just determined, is 6.4×10^{-5}, is, therefore, 4×10^{9} as strong a base as the parent substance, urea.

It is a base whose affinity is of the order of that of ammonia[4] ($K_{NH_4OH} = 1.8 \times 10^{-5}$).

Guanidine, the amide corresponding to the isourea ethers, is a very much stronger base, standing much closer to the alkalies than to the amines.[5]

Ethyl Isourea, $NH_2C(OC_2H_5):NH$.—Ethyl isourea hydrochloride was recrystallized twice from boiling absolute alcohol. An aqueous solution of the salt was neutral to sensitive litmus paper. The salt was dried for three days over concentrated sulphuric acid and solid potassium hydroxide, and its purity tested by a titration against tenth-normal silver nitrate, which gave 28.61 per cent. Cl. Calculated for $C_3H_8ON_2.HCl$, 28.43 per cent.

The conductivity measurements made with this salt at 25° are given in Table III.

TABLE III.

	Λv.		Λ_∞.	
v.	I.	II.	I.	II.
32	99.10	99.24	114.1	114.2
64	102.72	103.19	114.5	115.0
128	106.59	106.71	115.2	115.3
256	107.60	107.60	114.0	114.0
512	111.20	110.33	115.5	114.6
1024	[114.28]	[114.17]	[117.5]	[117.4]
Means (excluding $v = 1024$):			114.7	114.6

$$l_{\infty P} = 114.7 - 75.9 = 38.8.$$

The extreme molecular conductivity of the free base Λ_∞ is the sum of 38.8 and 195.8 (the extreme mobility of hydroxl ions), or 234.6.

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[1] *Ztschr. phys. Chem.*, **5**, 17 (1892).

[2] Walker (*J. Chem. Soc.* (London) **83**, (1903)), since this was written, has calculated the affinity constant of urea on the basis of a new set of more careful experiments and found $K = 1.5 \times 10^{-14}$. This value is so near the one calculated in the text that we have let the latter stand.

[3] The affinity constant of water, $K = \frac{C_H + C_{OH}}{C_{H_2O}}$ is one fifty-fifth of its dissociation constant, $K = C_H \times C_{OH}$.

[4] Bredig: *Ztschr. phys. Chem.*, **13**, 294, and foot-note p. 293 (1893).

[5] Ostwald: *J, prakt. Chem.*, **33**, 367.

The free base obtained according to the method of Stieglitz and McKee was tested for purity with the following result:

0.0902 gram substance required 10.15 cc. tenth-normal HCl. Calculated, 10.23 cc.

The conductivity measurements and the calculation of the affinity constant, K, follow:

TABLE IV.

	Λv.		100α.		10^5 K.	
v.	I.	II.	I.	II.	I.	II.
8	6.73	6.70	2.87	2.86	10.6	10.5
16	9.58	9.41	4.09	4.02	10.9	10.5
32	13.41	13.18	5.72	5.63	10.9	10.5
64	18.74	18.37	8.00	7.84	10.9	10.4
128	25.91	25.34	11.06	10.80	10.8	10.0
256	35.56	34.30	15.18	14.64	10.6	10.0
				Means:	10.8	10.3

Ethyl isourea is, therefore, nearly twice as strong a base as methyl isourea. It is interesting to observe that the substitution of an ethyl for a methyl group attached to oxygen has caused a much more decided increase in the affinity constant than is the case when a similar single substitution is effected for a methyl group attached to nitrogen (the constants for methyl and ethyl amine are 0.00050 and 0.00056 respectively).

Methyl Phenylisourea, $C_6H_5NHC(OCH_3):NH$.—Pure redistilled methyl phenylisourea was dissolved in absolute ether and a slight excess of dry hydrogen chloride added. The salt was washed with absolute ether and dried *in vacuo* over concentrated sulphuric acid and solid potassium hydroxide for several days. Its water solution was then neutral to sensitive litmus paper. The analysis gave 18.90 per cent. Cl. Calculated, 18.99 per cent.

The conductivity measurements made with this salt at 25° are given in Table V.

TABLE V.

		Λv.			$\Lambda \infty$.	
v.	I.	II	III.	I.	II.	III.
32	90.36	90.33	89.79	105.4	105.3	105.8
64	94.49	94.35	94.66	106.3	106.1	106.5
128	96.85	96.85	96.64	105.5	105.4	105.2
256	98.87	98.82	98.79	105.3	105.2	105.2
512	101.07	101.22	100.97	105.4	105.5	105.3
1024	102.55	102.67	102.40	105.7[1]	105.8	105.6
			Means:	105.6	105.6	105.6

$$l_{\infty P} = 105.6 - 75.9 = 29.7.$$

The extreme molecular conductivity of the free base, Λ_∞ is

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[1] It is noteworthy, but not unexpected, that in this case there is no abnormal increase of the molecular conductivity (see foot-note p. 459).

the sum of 29.7 and 195.8 (the extreme mobility of hydroxyl ions), or 225.5.

For the measurements of the conductivities of the free methyl phenylisourea, the latter was purified by two redistillations. The base, after it was dried for two days *in vacuo*, gave the following test for purity:

0.2627 gram substance required 17.54 cc. tenth-normal HCl. Calculated, 17.49 cc.

The measurements and the calculation of the affinity constant, K, follow:

TABLE VI.

	Λv.		100α.		10^5 K.	
v.	I.	II.	I.	II.	I.	II.
8	0.307	0.31	0.136	0.138	0.022	0.024
16	0.440	0.445	0.195	0.198	0.024	0.024
32	0.627	0.634	0.278	0.282	0.024	0.025
64	0.909	0.905	0.404	0.402	0.026	0.025
128	1.331	1.331	0.591	0.591	0.027	0.027
256	2.056	2.017	0.913	0.896	0.026	0.032
				Means:	0.025	0.026

The affinity constant of methyl phenylisourea is, therefore, only one-three hundredth that of methyl isourea. It is five hundred times greater than that of aniline[1] ($K = 5 \times 10^{-10}$). The determinations show that it is not sensibly[2] hydrolyzed in dilute solution and the neutrality to sensitive litmus paper and litmus solution confirms this view.

Ethyl Phenylisourea, $C_6H_5NHC(OC_2H_5):NH$.—Ethyl phenylisourea hydrochloride was prepared in exactly the same way as the methyl derivative. A water solution of the salt was neutral to sensitive litmus and a chlorine determination gave 17.76 per cent. Cl. Calculated, 17.57 per cent.

Table VII gives the conductivity measurements made with the salt at 25°.

TABLE VII.

	Λv.		Λ_∞.	
v.	I.	II.	I.	II.
32	88.70	89.38	103.7	104.4
64	92.86	92.86	104.8	104.7
128	95.90	95.90	104.5	104.5
256	97.51	97.51	103.9	103.9
512	99.67	100.15	104.0	104.4
1024	101.43	101.44	104.6	104.6
		Means:	104.1	104.6

$$l_{\infty P} = 104.3 - 75.9 = 28.4.$$

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[1] Bredig: *Loc. cit.*, p. 322.

[2] Within the limits of the sensitiveness of the measurements.

The extreme molecular conductivity of the free base, Λ_∞, is the sum of 28.4 and 195.8 (the extreme mobility of hydroxyl ions), or 224.2.

Ethyl phenylisourea was prepared, purified, and tested for purity exactly as the methyl derivative.

0.4806 gram substance required 29.30 cc. tenth-normal HCl. Calculated, 29.27 cc.

The measurements and the calculation of the affinity constant, K, follow:

Table VIII.

	Λ_v.		100α.		10^5 K.	
v.[1]	I.	II.	I.	II.	I.	II.
26.03	0.822	0.822	0.367	0.367	0.052	0.052
52.07	1.118	1.108	0.499	0.498	0.048	0.048
104.13	1.580	1.571	0.705	0.701	0.048	0.048
208.26	2.314	2.285	1.032	1.019	0.052	0.050
416.53	3.469	3.383	1.548	1.510	0.058	0.056
833.06	5.406	5.253	2.412	2.344	....	....
				Mean:	0.051 ;	0.051

Here again the substitution of the ethyl for the methyl group doubles the strength of the base.

For his interest, constant aid and advice, I wish here to express my great sense of obligation and gratitude to Professor Stieglitz.

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[Contribution from the Havemeyer Laboratories of Columbia University, No. 92.]

METAMINOBENZONITRILE AND SOME OF ITS DERIVATIVES.[2]

By Marston Taylor Bogert and Hal Trueman Beans.[3]

Received February 6, 1904.

A number of derivatives of orthoaminobenzonitrile and some of the para compound have been prepared but of those of metaminobenzonitrile only the chloride, chlorplatinate, nitrate, sulphate, and picrate are described in the literature.

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[1] An error was made in calculating the amount of the base necessary for a N/32 solution. The volumes, v, given are those actually used.

[2] Read before the New York Section of the American Chemical Society, at its meeting November 6, 1903.

[3] From the dissertation submitted by Mr. H. T. Beans in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.