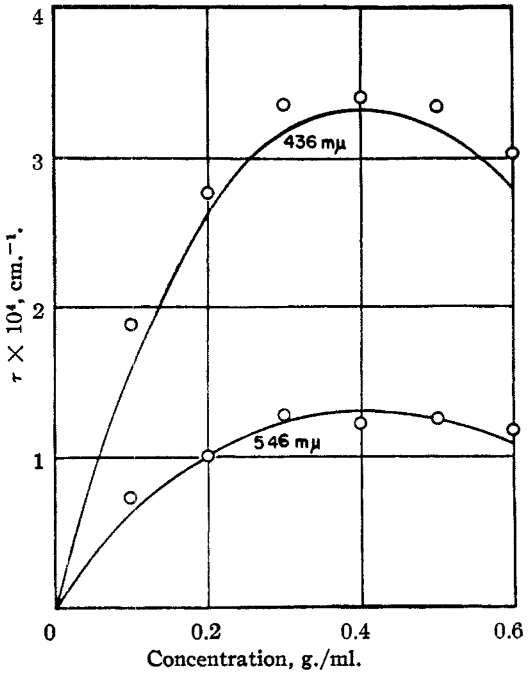

Fig. 1.—Turbidity of sucrose solutions *vs.* concentrations: the lines are the theoretical curves derived from osmotic pressure data. The points are experimentally determined turbidities.

For the former, the standard error of estimate was 2.16×10^{-4}; for the latter 0.825×10^{-4}. The cubic equation also predicts a turbidity maximum, although somewhat displaced from the correct value.

Slopes were obtained by differentiating the above empirical equation. Experimental turbidities, determined at 24–26°, were adjusted to 30° on the assumption that the turbidity is proportional to the absolute temperature.

The theoretical curve requires that the turbidity pass through a maximum at a concentration of about 0.4 g./ml. The experimental behavior conforms satisfactorily to the theory and constitutes a confirmation of it.

The decrease in turbidity when the concentration is increased beyond a certain point is most readily explained by assuming that, as the concentration increases, the randomness of the dilute solution gives way to an increasing degree of order. Increasing destructive interference of the light scattered by different molecules, with a resultant decrease in scattered light intensity, is the consequence. A point is finally reached beyond which increasing order more than balances the effect of increasing the number of scattering centers. A similar hypothesis has been advanced by Oster[12] to explain the decrease in turbidity of tobacco mosaic virus solutions with increased concentration beyond a certain point.

Summary

Absolute turbidities of solutions of pure sucrose have been determined up to a concentration of 0.6 g./ml. of solution. The turbidity increases with concentration, reaching a maximum at about 0.4 ml., then decreases. The theoretical turbidity curve derived from osmotic pressure data shows the same effect. The results confirm the validity of the theory.

[12] Oster, Doty and Zimm, THIS JOURNAL, **69**, 1193 (1947).

PHILADELPHIA 18, PA. RECEIVED JUNE 4, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Trifluoromethyl Hypofluorite

BY K. B. KELLOGG AND GEORGE H. CADY

During the past fifty years or more, several attempts have been made to prepare hypofluorous acid and hypofluorites using methods similar to those known to be successful for the corresponding compounds of chlorine. Fluorine behaves very differently from the other halogens, however, reacting with cold water to form hydrofluoric acid, hydrogen peroxide and a small amount of oxygen fluoride. With a dilute solution of sodium hydroxide it forms fluoride ion, oxygen, peroxide ion and some oxygen fluoride.[1] In view of these facts it appears possible that a more fruitful approach to the problem of preparing hypofluorites may be found in the direct fluorination of alcohols or other organic compounds to yield hypofluorites of the type ROF in which R is a perfluoro alkyl group. To test this possibility methyl alcohol has been fluorinated by two procedures recently reported for the complete fluorination of hydrocarbons.[2,3] One of the methods actually did produce trifluoromethyl hypofluorite, CF_3OF.

While this is the first compound which should obviously be named a hypofluorite, it is not the first substance to contain an O–F bond. Others possessing this bond are the oxygen fluorides, fluorine nitrate and fluorine perchlorate.

Experimental

One of the procedures was like that of Fowler, *et al.*,[2] who employed cobalt trifluoride as the oxidizing agent.

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[1] G. H. Cady, THIS JOURNAL, **56**, 1647 (1934).

[2] R. D. Fowler, W. B. Burford III, J. M. Hamilton, Jr., K. G. Sweet, C. E. Weber, J. S. Kasper and I. Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).

[3] G. H. Cady, A. V. Grosse, E. J. Barber, L. L. Burger and Z. D. Sheldon, *ibid.*, **39**, 290 (1947).

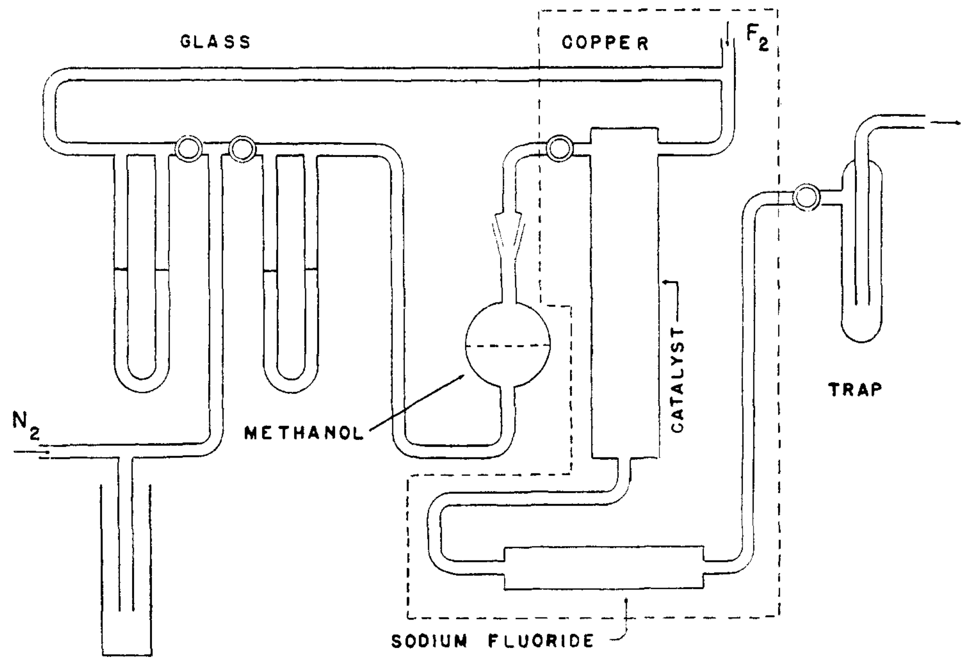

Fig. 1.—Catalytic system.

Results obtained by this method are presented later in the paper.

The other procedure was that of Cady, *et al.*[3] It comprised "catalytic" fluorination of methanol vapor by fluorine in the presence of a heated catalyst of copper ribbon coated with fluorides of silver. The reaction vessel, shown in Fig. 1, consisted of a copper tube of 7.5 cm. inside diameter and 90 cm. length. It was packed tightly with 4500 g. of copper ribbon of 0.035 cm. width and 0.008 cm. thickness having a total surface area of 150,000 sq.cm. In the preparation of the catalyst 100 g. of silver was deposited on the surface of the ribbon by displacement from a solution containing $Ag(CN)_2$ ion. Fluorine gas was later used to convert the silver to the difluoride. The reaction vessel was built in such a way that its temperature could be controlled by regulating the flow of electricity through two separate sections of nichrome ribbon used for electrical heating. When the system was in operation, a temperature between 160 and 180° was maintained. Streams of fluorine gas and methanol vapor, each diluted with dry nitrogen, were admitted separately into the top of the reaction chamber where they mixed in the presence of the catalyst. The gaseous products leaving the reaction vessel were passed through a tube containing sodium fluoride, used to absorb hydrogen fluoride, and then through a glass trap cooled by liquid oxygen. To ensure complete fluorination of the methanol, the respective flow rates of the entering gases were regulated to provide a large excess of fluorine. This condition was easily recognized by testing the action of the gas leaving the glass trap upon a piece of filter paper moistened with a solution of potassium iodide. Fluorine caused a rapid darkening of the paper as the result of liberation of iodine.

A straw-colored liquid together with a small amount of white solid material collected in the cold trap. This product was later fractionally distilled in a vacuum-jacketed column having a length of 75 cm., an internal diameter of 0.7 cm. and a packing of the type described by Bower and Cooke.[4] The gas flowing from the head of the column was passed through a series of sampling bulbs and then through apparatus for measuring the density of the gas by observing its flotation effect upon a glass bulb (Fig. 2). The most volatile fractions were of small volume. While the substances were not definitely identified, the properties observed corresponded to those of oxygen difluoride and carbon tetrafluoride. Following these materials came most of the product distilling under one atmosphere pressure at a temperature of $-97.0 \pm 0.5°$. This large cut had a nearly constant density corresponding in three different runs to weights of a molar volume of gas of 98, 97 and 97. Sample bulbs containing the product of constant boiling point were inverted into aqueous solutions of sodium hydroxide (1 *N*) and of potassium iodide. The reaction with the former produced oxygen while with the latter iodine was liberated. The free iodine was titrated with 0.1 *N* sodium thiosulfate. Two separate runs gave values of oxidizing equivalents per mole of 1.70 and 1.68. One molar volume of the product therefore liberated 0.85 mole of iodine.

While the observed density and oxidizing capacity were not those of any single compound which might have been expected to be present, they did correspond to a mixture of CF_3OF and COF_2 containing 85% by volume of the hypofluorite. Apparently an azeotropic mixture was obtained.

Carbonyl fluoride in the mixture was converted to carbon dioxide by allowing the gas to stand over water for three days. The remaining product was condensed and later distilled into another trap. After the liquid phase had distilled away, a white solid remained. This sublimed at about $-80°$ and had a molecular weight of 44. These data correspond to properties of carbon dioxide. The liquid phase was then fractionally distilled with the result that the principal product distilled under one atmosphere pressure at $-94.2 \pm 0.5°$. The density of the gaseous distillate remained nearly constant, corresponding to a weight of 103.5 g. for one molar volume. (Average values for two separate runs were 103.4 g. and 103.6 g.) Three determinations of the purified product gave values of oxidizing equivalents per mole of 1.980, 1.978 and 1.984. These data agree with the theoretical quantities for CF_3OF whose molecular weight is 104.0 and whose oxidizing capacity is two equivalents per mole of the hypofluorite.

The gas was next analyzed for its total fluorine content. A weighed amount of the gas was admitted to an evacuated Parr bomb containing some metallic sodium. This was heated over a Meeker burner for one hour to effect complete reaction of the gas with sodium. The contents of the bomb were then washed into a beaker and transferred to a

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(4) J. R. Bower, Jr., and L. M. Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

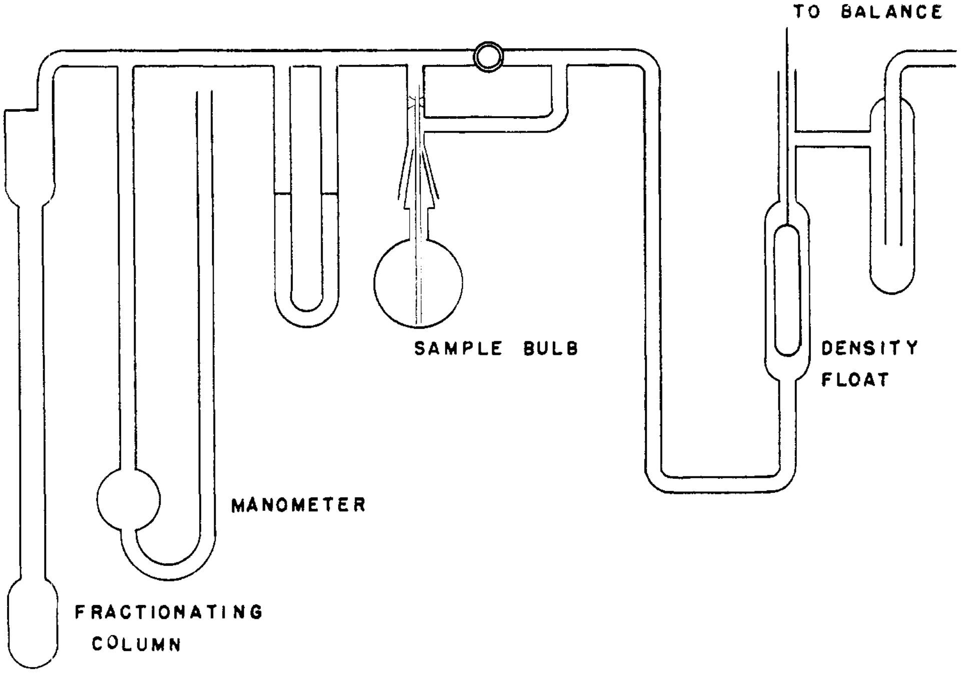

Fig. 2.—Purification system.

volumetric flask. Fluorine was determined by titrating an aliquot with standard 0.05 *N* thorium nitrate solution using sodium alizarin sulfonate indicator as described by Hoskins and Ferris.[5] The percentage of fluorine by weight was found to be 72.7, 73.5, 74.4, 73.2, 73.5 and 72.9 for six determinations which gave an average of 73.3%. The theoretical value for CF_3OF is 73.1%.

The true boiling point of the hypofluorite was determined from a series of vapor pressure measurements which were made using the apparatus shown in Fig. 3. The equipment consisted of a 60-ml. bulb connected to a condenser cooled with liquid oxygen. The whole of this assembly was contained in a strip-silvered Dewar flask. The bulb was heated by electricity to boil the compound and the temperature of the vapor immediately above the surface of the liquid was measured with a thermocouple located in a well running through the condenser and into the bulb. Vapor of the boiling hypofluorite filled the system up to a level a few mm. above the lower extremity of the condenser. Beyond this point the remainder of the system, including a mercury manometer, not shown in the diagram, was filled with dry air. A long coiled piece of glass tubing decreased the rate of diffusion of the hypofluorite into the part of the system used for measuring pressure and a tube containing solid potassium iodide and Drierite served to remove traces of CF_3OF which passed through the coil. A trap cooled by liquid oxygen was used as an added precaution to ensure the removal of gases which might react with mercury in the manometer. Each vapor pressure determination was made by holding the pressure within the system at a constant and known value until the corresponding boiling point of the liquid gave a constant reading with the thermocouple. Since the pressure could be easily set at any desired value, numerous measurements were made between pressures of 4.40 and 176.7 cm. of mercury. The data for two samples of the compound were found to be the same and no change was observed when about half of one of the samples was removed.

The relationship between vapor pressure and absolute temperature is given by the equation

$$\log P_{(\mathrm{cm.})} = 6.0059 - \frac{656.22}{T} - \frac{13988}{T^2}$$

The probable experimental deviation of an observed value of log *P* from this equation was

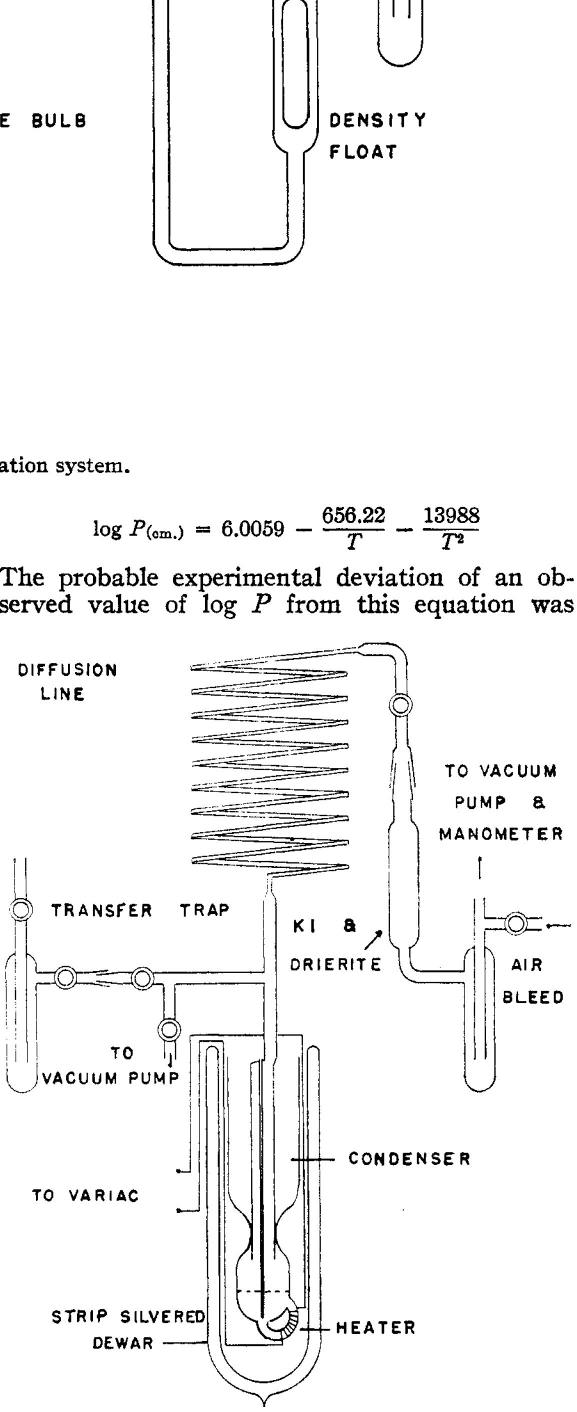

Fig. 3.

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[5] W. M. Hoskins and C. A. Ferris, *Ind. Eng. Chem., Anal. Ed.*, **8**, 6 (1936).

±0.0025. The curve (Fig. 4) plotted from the experimental data indicates a boiling point of 95.0°

Table I gives a comparison of some observed vapor pressures with those calculated from the equation.

TABLE I

T, °C.	$P_{\text{exp.}}$, cm.	$P_{\text{calcd.}}$, cm.
144.7	6.30	6.33
153.5	13.92	13.76
158.3	20.22	20.09
165.9	34.82	34.85
178.2	76.09	76.46
188.9	137.50	137.96
193.9	176.70	177.27

The heat of vaporization was calculated using the unintegrated form of the Clapeyron equation. The ΔV term was obtained by assuming the vapor to be an ideal gas and the liquid to have a molar volume of 55 cc. This volume corresponded to a crudely determined density of 1.9 g./cc. of liquid. A value of 3710 cal./mole was obtained for the heat of vaporization at the boiling point under one atmosphere pressure.

Fluorination of methanol by cobalt trifluoride did not yield trifluoromethyl hypofluorite. When methanol vapor, diluted with nitrogen, was passed through the reaction chamber at 180 to 200° the product was a mixture consisting principally of hydrogen fluoride and carbonyl fluoride. A little carbon tetrafluoride was also produced when the reaction chamber was held at about 250°.

Since trifluoromethyl hypofluoride was produced by the catalytic technique but not by fluorination with cobalt trifluoride, it was suspected that silver difluoride might react alone with methyl alcohol vapor to form the hypofluorite. This idea was shown to be incorrect, however, by causing the alcohol vapor to react with silver difluoride at about 170°. The product contained only hydrogen fluoride, carbonyl fluoride and carbon dioxide. Apparently the presence of free fluorine was required for production of the hypofluorite. It was found, however, that either carbon monoxide or carbonyl fluoride would react with fluorine in the catalytic chamber to form the hypofluorite. Although carbon monoxide is the best starting material, because of its low fluorine requirement, most of the hypofluorite produced for this research was prepared from methanol. The yield for the alcohol and carbon monoxide were about 50 and 70%, respectively, of those theoretically possible from the amount of the carbon compound consumed.

A number of reactions of the hypofluorite were studied in order to get a measure of its reactivity. The gas readily liberated both bromine and iodine from solutions of their salts, but it reacted only very slowly with a solution of sodium chloride. It displaced chlorine rapidly from solid sodium chloride at a temperature of about 150°. When the gas was passed through an acidified solution of potassium iodide, it reacted vigorously with the evolution of much heat and liberation of iodine. The products contained both carbonyl fluoride and carbon dioxide, probably formed by reactions (1) and (2).

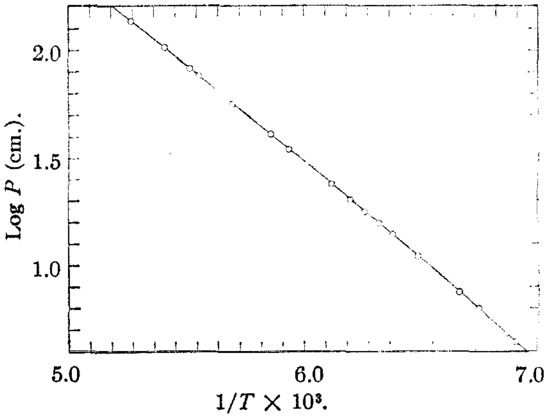

Fig. 4.—Vapor pressure curve.

$$CF_3OF + 2I^- + 2H^+ \longrightarrow COF_2 + I_2 + 2HF \quad (1)$$

$$COF_2 + H_2O \longrightarrow CO_2 + 2HF \quad (2)$$

When a sample of the gas reacted at room temperature with a 1 N solution of sodium hydroxide, one volume oxygen was produced for each two volumes of CF_3OH consumed.

$$2CF_3OF + 12OH^- \longrightarrow O_2 + 2CO_3^= + 8F^- + 6H_2O \quad (3)$$

The presence of $CO_3^=$ was shown by acidifying the solution and testing the evolved gas for CO_2.

An attempt was made to produce trifluoromethyl alcohol, CF_3OH, by treating the hypofluorite with hydrogen. The reaction was carried out at about 160° by passing an equimolar mixture of the gases through a vessel filled with copper ribbon. Upon analysis of the products only carbonyl fluoride, hydrogen fluoride and a trace of carbon dioxide were found. The amount of hydrogen fluoride corresponded to two moles per mole of hypofluorite consumed. This evidence shows that the reaction was

$$CF_3OF + H_2 \longrightarrow COF_2 + 2HF \quad (4)$$

The hypofluorite was found to react very slowly with water forming carbon dioxide. The gas did not react with glass at room temperature, but when Pyrex glass tubing was heated to its softening point, it was attacked.

An attempt was made to measure the freezing point of the hypofluorite by cooling the liquefied gas with liquid nitrogen boiling under vacuum. However, the substance did not solidify even at the lowest temperature reached, −215°.

The stability of the substance toward heat was demonstrated by passing a sample through a copper tube heated to about 450°. The gases flowing from the tube passed into a trap cooled by liquid oxygen. This procedure should have allowed any fluorine set free by decomposition of the compound to pass through the trap without being condensed. No fluorine was observed, however, and the material which collected in the trap was trifluoromethyl hypofluorite.

Discussion

The fluorination of methanol vapor in the catalytic chamber may occur by the following steps.

$$6AgF_2 + CH_3OH \longrightarrow 6AgF + COF_2 + 4HF \quad (5)$$
$$COF_2 + F_2 \longrightarrow CF_3OF \quad (6)$$
$$2AgF + F_2 \longrightarrow 2AgF_2 \quad (7)$$

There is no reason to feel that these equations represent the actual mechanism of the reaction. Step (5) is obviously a complex change which may involve the formation of CF_3OH with subsequent decomposition into COF_2 and HF. It is also possible that a part of the hypofluorite may be formed by the replacement of hydrogen in methanol without passing through the intermediate compound, COF_2.

Acknowledgment.—This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

Summary

The compound, trifluoromethyl hypofluorite, CF_3OF, has been produced by fluorinating methyl alcohol, or carbon monoxide, in the presence of silver difluoride and fluorine. The substance is a gas having an odor similar to that of fluorine or oxygen fluoride. When liquefied, it has a pale straw color, and the liquid boils under one atmosphere pressure at a temperature of −95.0° The gas is stable up to 450° and is a strong oxidizing agent of high reactivity.

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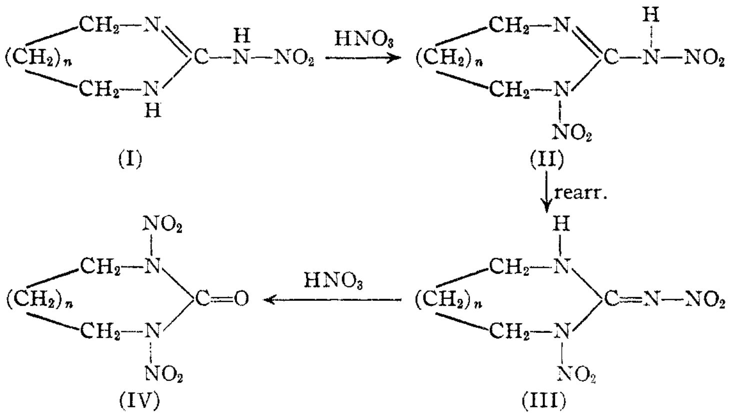
[Contribution from the Chemical Laboratory, University of Toronto]

The Nitration Products of 2-Nitramino-Δ²-1,3-diazacycloalkenes

By A. F. McKay and George F Wright

Although guanidine and many monosubstituted guanidines may be nitrated at the primary amido group, no di- or trisubstituted nitroguanidine has heretofore been prepared. Thus the nitro derivatives of *sym.* dimethyl, trimethyl or triethylguanidine, and also of N-alkyl-N′-nitroguanidines are unknown.[1,2] In the present work the resistance of *sym.* dibutylguanidine and triethylguanidine toward nitration has been demonstrated under our experimental conditions. This resistance to nitration is probably not owing to base strength,[1,3] since guanidine and trimethylguanidine are comparable proton-donors. Davis and Elderfield originally noted this and then decided on the basis of the available data that a primary amido group was necessary for the nitration process.

This restriction is no longer valid since we have found it possible to nitrate 2-nitramino-Δ²-imidazoline,[4] I ($n = 0$). This reaction can be carried out, like the nitration of guanidine, in mixed acid at −10° or by treating the nitrate salt with sulfuric acid. The product, 1-nitro-2-nitramino-Δ²-imidazoline, II ($n = 0$), may also be obtained by treatment of I with one equivalent of nitric acid in acetic anhydride, but 1,3-dinitroimidazolidone, IV ($n = 0$), is produced instead when an excess of nitric acid is used in acetic anhydride. This latter result is not surprising because the nitration product, II ($n = 0$), can be converted to the cyclic urea, IV, when it is treated with an excess of nitric acid.



An adequate explanation may be suggested as an allylic rearrangement of hydrogen in II ($n = 0$) to give III ($n = 0$). This substance, a nitrimine, might be expected to lose nitrous oxide with great ease[5,6] during nitration, ultimately to yield IV ($n = 0$).

The nitration of 2-nitramino-Δ²-1,3-diazacyclohexene, I ($n = 1$), and 2-nitramino-Δ²-1,3-diazacycloheptene, I ($n = 2$), did not proceed so

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(1) T. L. Davis and R. C. Elderfield, This Journal, **55**, 731 (1933).

(2) A. F. McKay and G. F. Wright, *ibid.*, **69**, 3028 (1947).

(3) G. E. Dunn, J. C. MacKenzie and G. F. Wright, *Can. J. Research*, **26**, 104 (1948).

(4) A. F. McKay and G. F. Wright, This Journal, **70**, 430 (1948).

(5) G. S. Myers, J. W. Suggitt and G. F. Wright, *J. Org. Chem.*, **12**, 373 (1947).

(6) G. N. R. Smart and G. F. Wright, *Can. J. Research*, **26B**, 284 (1948).