the warming curve, the heat of formation of $D_{1.3.16}$ is approximately 1100 kcal.

The complex $D_{3\cdot4\cdot16}$ was prepared in a similar manner. A simple warming experiment showed no evidence of decomposition below approximately 100°, at which temperature some water loss

occurred.

The authors wish to express their appreciation to Shell Development Company for permission to publish this work, and to R. C. Hurlbert for assistance in evaluation of the heat of formation of $D_{1\cdot3\cdot16}$.

REACTION OF ACTIVE NITROGEN WITH METHYL CYANIDE¹

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Received May 21, 1956

The reaction of active nitrogen with methyl cyanide was studied at five temperatures in the range 90 to 460°. The main products were hydrogen cyanide and hydrogen. Smaller amounts of cyanogen, methane, ethane, ethylene, acetylene and (probably) methylisonitrile were also recovered. The yields of primary products, in relation to the methyl cyanide flow rate, indicate complete consumption of active nitrogen at each temperature, but the maximum yield increased markedly with increase of temperature.

Introduction

Previous studies in this Laboratory have shown that, although reactions of active nitrogen with hydrocarbons yield mainly hydrogen cyanide, small amounts of cyanogen may also be formed. The present study was made to determine whether, with the CN group present in methyl cyanide, reaction of this molecule with active nitrogen would reveal another aspect of active nitrogen reactions that might be useful in their interpretation.

Experimental

The apparatus was similar to that described in an earlier paper.³ The molecular nitrogen flow rate was 5.98 $\times 10^{-5}$ mole/sec., corresponding to an operating pressure of 1.03 mm. in the system. Methyl cyanide "chemically pure" was purchased from Brickman and Company, Montreal, and was purified as outlined previously.³

Condensable products of the reaction were distilled into a low temperature still of the type described by Le Roy.⁴ The C₂ hydrocarbons were distilled at -140° and analyzed on a mass-spectrometer.⁵ The excess of the reactant and the products were condensed on N/2 KOH frozen in liquid nitrogen. Upon melting, the solution was divided into three aliquots. In one aliquot, total cyanide (= a) was determined by titration with silver nitrate⁶; the second aliquot was acidified with dilute sulfuric acid (1:10) and boiled $\frac{1}{2}$ hour. The ammonia so formed (= b) was determined by Kjeldahl distillation. The third aliquot was transferred into a tube, frozen in liquid nitrogen, and an equal volume of concentrated sulfuric acid slowly added. The tube was then evacuated, sealed and digested for 12 hours at 150°. Total ammonia (= c) was then determined in another Kjeldahl distillation. Cyanogen (= d) was determined in a separate experiment by the method of Rhodes.⁷ Net hydrogen cyanide was given by the difference (a - d), and unreacted methyl cyanide by (c - a - b). In the absence of any reaction products easily hydrolyzable by dilute acids, the determination of cyanogen as ammonia (b), or by the direct method (d) should have yielded identical results. However, the result (b) was consistently higher than the result (d), and the discrepancy was attributed to

(1) With financial assistance from the National Research Council of Canada.

(2) Holder of National Research Council Bursary and Studentships, 1952-1955.

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(5) The authors are indebted to Dr. H. I. Schiff for permission to use the mass spectrometer, and to Dr. D. Armstrong for the analyses.

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the presence of methylisonitrile in the reaction products. Methylisonitrile was identified by its hydrolytic products, *i.e.*, methylamine and formic acid, which were detected in the acidified reaction mixture by tests due to Valton⁸ and Grant,⁹ respectively. No attempt was made to determine the methylisonitrile quantitatively, in view of the small amounts involved (at most 3% of total products at 235°). The difference (b - d) was assumed to represent methylisonitrile, and the carbon and hydrogen balances calculated on this basis were between 99 and 101%.

Non-condensable reaction products were withdrawn from the nitrogen stream with a Toepler pump and analyzed on the mass spectrometer.

Experiments were made at 90, 160, 245, 345 and 460°.

Results

The results for all the products exclusive of methane are summarized in Figs. 1, 2 and 3. No methane was found at 90°; the results of analyses at 460° were:

MeCN flow rate, mole/sec. × 10°	Methane yield, mole/sec. \times 10°
3.5	0.00
8.1	.00
15.5	. 184

The data for methylisonitrile are uncertain, *i.e.*, the amounts calculated might represent methylisonitrile plus other unidentified components. At lower temperatures these results were fairly reproducible, but at 345 and 460° the reproducibility became very poor and no consistent data could be obtained.

Discussion

In discussing the results, the assumption will be made that the reactive species in active nitrogen is atomic nitrogen in the ground state, for reasons indicated elsewhere.¹⁰

Since the main products of the reaction were hydrogen and compounds containing a carbonnitrogen bond, it would appear that the initial attack of the nitrogen atom was at a carbon atom in the methyl cyanide molecule. Seven possible

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reactions may be suggested, of which three are highly endothermic and a fourth¹¹ may be ruled out on evidence available. The only three exothermic reactions are all spin disallowed.^{10a} They are¹²

$$N + CH_{3}CN \longrightarrow 2HCN + H + 19 \text{ keal.}$$
(1)

 $N + CH_3CN \longrightarrow C_2N_2 + H_2 + H + 7 \text{ kcal.}$ (2)

 $N + CH_{3}CN \longrightarrow HCN + CN + H_{2} + 9 \text{ kcal.}$ (3)





(11) The reaction N + CH₂CN \rightarrow CH₂C + N₂ + ? kcal. seems unlikely since studies in this Laboratory have shown that no C₂ hydrocarbons are formed when active nitrogen is introduced into excess hydrogen cyanide; H. Brody, M. Sc. thesis, McGill University, 1955.

(12) The approximate heats of reaction were calculated from heats of formation published by the National Bureau of Standards in "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Washington, 1952, supplemented by

Heat of

Substance	formation (kcal./ mole)	Reference
CN	-93	L. Brewer, L. K. Templeton, and
		F. A. Jenkins, J. Am. Chem. Soc.,
		73, 1462 (1951); C. A. Me-
		Dowell and J. W. Warren,
		Trans. Faraday Soc., 48, 1084
		(1952).
N	-112	A. E. Douglas, This Journal, 59,
		109 (1955).
CH₂CN	-70	Rough estimate



Fig. 2.—Dependence of cyanogen and isonitrile (?) yields on methyl cyanide flow rate (symbols have same significance as in Fig. 1).



Fig. 3. Dependence of acetylene, ethylene and ethane yields on methyl cyanide flow rate (symbols have same significance as in Fig. 1).

All three reactions will produce the entities H and CN in the ratio 3:2, *i.e.*, three hydrogen atoms are formed for every two CN radicals when no attention is paid to the state of combination. A simple material balance requires that the yield of final products in each case must obey the relation

(yield of H_2) = $\frac{1}{4}$ (yield of HCN) + $\frac{3}{2}$ (yield of C_2N_2)

Inspection of Figs. 1 and 2 shows that this relation is approximately satisfied at both 90 and 460° . The agreement obviously means only that any one of the three reactions, or any combination of them, is not inconsistent with the experimental results.

It has not been possible to assess the relative importance of reactions 1, 2 and 3 except by comparison with the reaction of active nitrogen with methyl chloride.¹³ In that reaction, neither cyanogen chloride nor chlorine was found among the products. By analogy, it might be inferred that the production of HCN in reaction 1 is probably large compared with the extent of its formation in reaction 3, or through C_2N_2 and CN produced in reactions 2 and 3, respectively.

The plateaus on the curves of Figs. 1, 2 and 3 indicate that, irrespective of mechanism assumed, the amounts of the primary products formed in the initial step (or steps) remain constant above a certain critical flow rate of methyl cyanide at each temperature. The only explanation seems to be that all the available nitrogen atoms are consumed when the methyl cyanide flow rate exceeds the critical values, and that the number of nitrogen atoms participating in product formation is quite different at different temperatures. Similar though less accentuated behavior has been observed in the reaction of methyl chloride with active nitrogen.¹³ The observation can be explained if it is assumed that the reactant acts as an efficient catalyst for the recombination of nitrogen atoms; a mathematical analysis of the problem is projected for a further publication.

The ethane found in the reaction products at higher temperatures, and at methyl cyanide flow rates above the critical values, presumably resulted from recombination of methyl radicals formed³ in the reaction

$$H + CH_3CN \longrightarrow HCN + CH_3$$
 (4)

At lower methyl cyanide flow rates, where nitrogen atom consumption was incomplete, methyl radicals should be destroyed rapidly¹⁴ and ethane production correspondingly insignificant, as observed.

The few data for methane content of the products suggest that the pattern of methane production was similar to that for ethane and that methane also resulted from reactions of methyl radicals

$$CH_3 + H \longrightarrow CH_4$$
 (5)

$$CH_3 + H_2 \longrightarrow CH_4 + H$$
 (6)

$$CH_3 + CH_8CN \longrightarrow CH_4 + CH_2CN$$
 (7)

Reactions 6 and 7 are known to have activation

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(14) D. A. Armstrong and C. A. Winkler, ibid., 33, 1649 (1955).

energies of about 10 kcal.^{15,16} and should occur at appreciable rates at 345° and 460°. Hence, reactions 4 and 6 could lead to methyl radical production by a chain mechanism. This apparently does not occur, however, since the straight lines representing the production of ethane (Fig. 3) do not have a common origin nor do they have different slopes at different temperatures, corresponding to different extents of a chain reaction. In the absence of a chain reaction, there should be a methyl cyanide flow rate above which ethane production from recombination of methyl radicals should become constant. Apparently this flow rate was not attained for the conditions of the present experiments. Further, the recovery of ethane at 460° at a lower methyl cyanide flow rate than at 345° may be attributed to an increase, with temperature, of the rate of reaction 4, and may also indicate that there is more rapid consumption of nitrogen atoms at the higher temperature.

The pattern of acetylene production (Fig. 3) suggests that acetylene is a primary product from the attack of active nitrogen on methyl cyanide. It seems necessary to assume that acetylene is formed in a drastic disruption of the methyl cyanide molecule, perhaps in a sequence such as

$$CH_3CN + N \longrightarrow CH_3CN \cdot N$$

 $CH_3CN \cdot N + N \longrightarrow N_2 + reactive fragments$

which would be expected to accompany catalyzed recombination. The recombination of two nitrogen atoms makes available more than 200 kcal. and there should be a good chance that the methyl cyanide part of the complex receives enough energy to dissociate into reactive fragments. Among the possible fragments are CH, CH₂, CH₃ and CN. Acetylene might then result from recombination of CH radicals, or from interradical reactions such as¹⁷

$$CH_2 + CH_3 \longrightarrow C_2H_2 + H_2 + H$$

The presence of ethylene in the products may also be explained by interaction of radicals formed by fragmentation of the parent molecule, *e.g.*

$$2CH_2 \longrightarrow C_2H_4$$
$$CH + CH_3 \longrightarrow C_2H_4$$

At low methyl cyanide flow rates, some of the fragments might be involved in subsequent reactions, such as

$$\begin{array}{ccc} CH_2 + N \longrightarrow CN + H_2 \\ CH + N \longrightarrow CN + H \end{array}$$

It seems reasonable to assume that some of the CN radicals produced directly or indirectly in the fragmentation of the methyl cyanide molecule should recombine to cyanogen. If these fragments were the only source of cyanogen, the following relation might be expected at high methyl cyanide flow rates and at low temperatures

$\mathrm{C_2H_2} + \mathrm{C_2H_4} \geq \mathrm{C_2N_2}$

The fact that this relation is not satisfied (Figs.

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(17) H. Wiener and M. Burton, J. Am. Chem. Soc., 75, 5815 (1953).

2 and 3) suggests that reactions 2 and 3 may contribute appreciable cyanogen to the products.

sion reaction of the type reported by Ogg and

Polanyi¹⁸

 $CN + CH_3CN \longrightarrow CH_3NC + CN - 15$ kcal.

The formation of some methylisonitrile in the methyl cyanide-nitrogen atom reaction is difficult to explain. It might arise from a reaction between CH₃ and CN radicals, or conceivably from an inver-

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FORMATION CONSTANTS OF SOME METAL DERIVATIVES: S-ALKYL CARBOXYLIC ACIDS

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Contribution from The College of Chemistry and Physics, The Pennsylvania State University, University Park, Pennsylvania Received May 21, 1956

Formation constants are reported for the compounds $C_2H_5SCH_2COOH$, $C_2H_5SCH_2COOH$ and $o-C_2H_5SC_{6}H_4COOH$ with the following metals: Cu, Ni, Pb, Cd, Co, Zn, Mg. The order of stability for the metal derivatives of a given ligand is different in some respects from that previously established for coördination through oxygen and/or nitrogen. Fivemembered chelate rings are more stable than six-membered rings. For these sulfur-containing ligands log $K_2 > \log K_1$ with some metals, in contrast to the situation usually found for ligands coördinating through oxygen, nitrogen and oxygen, and nitrogen and sulfur. Difficulties encountered in the study of sulfur compounds are discussed.

Introduction

Since 1941 a good deal of information has accumulated on the relative stabilities of metal coördina-tion compounds.²⁻⁵ The data demonstrate the existence of several regularities among the properties of coördination compounds.⁵⁻⁸ However, if one lists the ligand molecules or anions for which data on formation constants exist, one sees that these ligands all coördinate through the atoms oxygen and nitrogen: oxygen only, β -diketones, ohydroxyaldehydes, tropolone, hydroxyquinones, kojic acid, etc.; nitrogen only, diamines, polyamines, o-phenanthroline, dimethylglyoxime, etc.; oxygen and nitrogen simultaneously, amines con-taining -O- and -OH, 8-quinolinol, amino acids, the "complexones," o-hydroxy azo dyes, etc. Although many familiar ligands coördinate through sulfur, very few data on formation constants exist for such ligands: sulfur only apparently none; sulfur and nitrogen simultaneously, amines containing -S- and -SH, 9,10 o-aminobenzenethiol11; sulfur and oxygen simultaneously, o-mercaptobenzoic acid.¹² Furthermore, these data are not suffi-

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(11) R. C. Charles and H. Freiser, J. Am. Chem. Soc., 74, 1383 (1952).

(12) T. Foley and R. C. Anderson, *ibid.*, **70**, 1195 (1948); **71**, 909 (1949); **72**, 5609 (1950); R. C. Anderson and S. E. Turner, *ibid.*, **71**, 912 (1949).

ciently numerous to permit one to judge whether the same regularities which hold for coördination through oxygen and nitrogen, are valid for coordination through sulfur. The present report is a preliminary account of an investigation begun in an effort to furnish formation constant data for sulfurcontaining ligands.

Experimental

S-Ethylmercaptoacetic Acid, $C_2H_4SCH_2COOH$.—This compound was obtained by the action of ethyl mercaptan on monochloroacetic acid in alkaline solutions¹³: pale yellow liquid with an unpleasant odor; b.p. 117° at 11 mm., d^{20}_4 1.152; lit. values b.p. 117.8° at 11 mm., d^{20}_4 1.1518, 90% yield.

β-(S-Ethylmercapto)-propionic Acid, $C_2H_5SCH_2COOH$. —β-Chloropropionic acid (5.5 g.) was dissolved in 10 ml. of water containing 2.5 g. of sodium hydroxide. To the cooled solution (ice-bath) was added with constant stirring an icecold solution of 3.5 ml. of ethyl mercaptan and 2.5 g. of sodium hydroxide in 5 ml. of water. After the mixture was allowed to stand at room temperature for several hours, it was again cooled in ice and carefully made acid to litmus with 20% sulfuric acid. The solution was repeatedly extracted with ether, and the extract dried over calcium chloride. After removal of the ether, the oil was distilled *in vacuo* to yield a pale yellow oil soluble in water and readily soluble in dioxane; b.p. 127° at 12 mm., d^{20}_4 1.143, n^{25} D 1.482, yield 3.8 g. (68% based on chloropropionic acid), neut. equiv., 134.0 g., theoretical 134.2 g., molar refraction 3.46 cc., caled. 33.42 cc.

o-(S-Ethylmercapto)-benzoic Acid, $C_2H_bSC_eH_4COOH.$ — Thiosalicylic acid (7.2 g.) was added to a solution of 5 g. of sodium hydroxide in 10 ml. of water and 50 ml. of alcohol. This mixture was refluxed with 3.9 ml. of ethyl iodide for 2 hours. On cooling and acidification with dilute hydrochloric acid (litmus as indicator) the compound separated as a white powder.¹⁴ It was recrystallized twice from water; yield 95%, m.p. 135°; lit. value 134–135°. 2,3-Dimercaptopropanol was purchased from the Delta Chemical Works. Mercaptoacetic acid, cysteine hydrochloride, and methionine were obtained from Distillation Products Inducting Dioxano gas purified by Eigen

2,3-Dimercaptopropanol was purchased from the Delta Chemical Works. Mercaptoacetic acid, cysteine hydrochloride, and methionine were obtained from Distillation Products Industries. Dioxane was purified by Eigenberger's procedure¹⁵ and stored over activated alumina in a brown bottle to minimize the formation of oxidizing decomposition products on standing.

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