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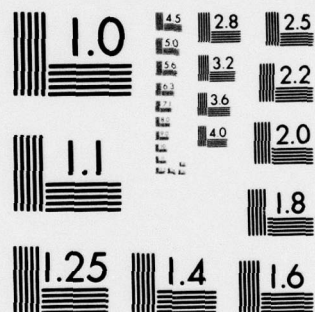
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"FIXATION OF NITROGEN WITH AQUEOUS ATOMIC NITROGEN"

FINAL REPORT

BY

NORMAN N. LICHTIN

FEBRUARY 28, 1977

U. S. ARMY RESEARCH OFFICE

GRANT DA-AROD-31-124-27 G195

FOR THE PERIOD JUNE 15, 1972 - DECEMBER 31, 1977

TO

BOSTON UNIVERSITY



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Planned research involved fixation of nitrogen in organic compounds in reactions of potential synthetic utility in which active nitrogen, mostly $N(^4S)$, acted on organic solutes dissolved in water or other unreactive polar solvents. A previously reported conversion of aqueous ethanol to acetamide could not be repeated. HCN(10-30 mole percent) and NH_3 (0-4 mole percent) were the only identified nitrogenous products of the reaction with aqueous or neat liquid methanol or ethanol. Molecular decomposition to H_2 , $(CH_2OH)_2$ and CH_2O is the principal process with CH_3OH . Product yields, their dependence on → next page		

20. Abstract (continued)

cont

concentration of FeCl_3 , EPR spectra of radicals trapped with phenyl-*t*-butyl nitron and isotopic composition of hydrogen produced from CH_3OD show that free H atoms and CH_2OH radical are only minor precursors of observed products formed from neat MeOH at -79°C . Products are similar whether $\text{N}(^4\text{S})$ is introduced by rapid bubbling beneath the surface or impinged upon it but dissolved FeCl_3 does not affect yields in the latter case. More limited data obtained with ethanol present a similar picture. The data suggest that energy released upon recombination of nitrogen atoms at or near the gas-liquid interface induces decomposition of methanol or ethanol in localized regions similar to "spur" regions which characterize radiolysis of water.

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I. OBJECTIVES OF RESEARCH

Planned research consisted of a study of reactions of active nitrogen, largely $N(^4S)$, (produced by a microwave-supported glow discharge in N_2) with organic compounds in solution in liquid water or other unreactive solvents. The objective was to identify nitrogen fixation reactions of potential synthetic utility and to investigate chemical mechanism of one or more such reactions. The basis for this objective was the prior observation in our laboratory (1) that active nitrogen converted 1-10M

1. C. T. Chen and N. N. Lichtin, J. Amer. Chem. Soc., 93, 5922 (1971).

aqueous ethanol to acetamide with a fixation efficiency of $\sim 60\%$, i.e., the yield of CH_3CONH_2 corresponded to $\sim 60\%$ of the $N(^4S)$ in the gas stream bubbled through the solution.

II. RESEARCH RESULTS

Independent work by three different investigators in this laboratory (Drs. D. Levy, M. J. Brooks and V. Franchetti) failed to repeat the reported conversion of ethanol to CH_3CONH_2 . The reason for these discrepant results remains unknown. The reactions of aqueous methanol (2)

2. C. T. Chen and N. N. Lichtin, J. Amer. Chem. Soc., 92, 7506 (1970).

and ethanol with active nitrogen were therefor reinvestigated and the reactions of the neat liquid alcohols were studied extensively. In all cases, HCN was found to be the only product of fixation of nitrogen formed in substantial amounts, i.e., of the order of 10 to 30 molecules per 100 atoms of $N(^4S)$ incident. Under some conditions, smaller amounts of NH_3 , e.g., 1 to 4 molec/100 atoms of $N(^4S)$ was formed. No other nitrogenous

products were identified. The remaining identified products included glycols, aldehydes and H_2 . Since it appeared that the original goal of the project could not be realized, the effort was redirected towards elucidation of mechanism of formation of the observed products.

In addition to identification of products, experiments included measurement of product yields from aqueous solutions of varying concentration and from the neat alcohols over a range of temperatures from -16 to $-91^\circ C$. Active nitrogen was introduced by bubbling beneath the surface of bulk liquid or by impinging upon the surface. In some experiments, reaction took place in the gas phase or reactants were mixed in the gas phase and bubbled beneath the surface of bulk liquid. The effect of a wide range of concentrations of $FeCl_3$ on yields of products was investigated. The isotopic concentration of molecular hydrogen produced by the reaction of neat liquid CH_3OD at -79° was determined. The EPR spectra of radicals formed by addition to phenyl-t-butyl nitron during the reaction of active nitrogen with neat liquid CH_3OH were measured.

The major organic products from neat liquid methanol at $-79^\circ C$ are $(CH_2OH)_2$ and CH_2O . Correspondingly, $(CH_3CHOH)_2$ and CH_3CHO are formed from ethanol along with smaller amounts of $(CH_2CH_2OH)_2$, $CH_3CHOHCH_2OH$ and CH_2O . H_2 is the product formed in largest yield from methanol. (The yield of H_2 from ethanol was not studied, nor were yields of CO measured.) Quantitative data are summarized in Tables 1-8. Hydrogen produced from CH_3OD consisted of approximately equal amounts of H_2 and HD but D_2 was not detectable. Spin trapping experiments indicated that both H atoms and $\dot{C}H_2OH$ radicals are produced from CH_3OH . However, the effect of $Fe(III)$ on

yields of H_2 , glycols and aldehydes produced in experiments where active nitrogen was bubbled beneath the liquid surface, as well as other data, indicated that only a minor fraction of the observed products were formed by reactions of free radicals in the bulk. Yields were not influenced significantly by $Fe(III)$ when the stream of active nitrogen was impinged on the surface of either methanol or ethanol.

III. CONCLUSIONS

All data now at hand appear to be consistent with chemical changes originating largely in molecular decomposition in localized regions caused by the deposition at or near the gas-liquid interface of either the entire energy of recombination of nitrogen atoms, 225 Kcal/mole, or of the decay energy of $N_2(A^3\Sigma_u^+)$, 142 Kcal/mole in the $v=0$ state. The proposed localized regions of energy deposition resemble the "spur" regions which are well known in the radiolysis of water.

A more detailed statement of some of our data and the basis for our conclusions is presented in reference 1 of the bibliography which follows in section V. A copy of this preliminary publication is included in this report. A complete article is in preparation and will be submitted to ARO when it is available.

IV. TABLES OF DATA

Table 1

ACTIVE NITROGEN BUBBLED THROUGH AQ. MeOH AT $5 \pm 3^\circ C$

<u>[MeOH]</u> <u>M</u>	<u>$10^2 \times$ Moles of Product/g Atom of N</u>				<u>$N(^4S)$</u>
	$(CH_2OH)_2$	CH_2O	HCN	NH_3	μ mole/sec
2	$3.7 \pm .2$	3.8 ± 1.9	14.5 ± 1.6	$1.2 \pm .3$	1.8
5	$3.6 \pm .2$	5.5 ± 2.2	15.8 ± 3.0	$1.2 \pm .2$	$1.8 \pm .2$
10	$2.8 \pm .8$	12.2 ± 2.8	25.8 ± 2.4	$2.0 \pm .3$	$1.8 \pm .2$
15	$3.2 \pm .3$	8.7 ± 1.6	18.8 ± 2.9	$1.4 \pm .4$	$2.0 \pm .1$

Table 2

ACTIVE NITROGEN BUBBLED THROUGH NEAT LIQUID MeOH

Temp	$10^2 \times \text{Moles of Product/g Atom of N}$					$N(^4S)$
°C	$(CH_2OH)_2$	CH_2O	HCN	NH_3	H_2	$\mu\text{mole/sec}$
-16	$4.2 \pm .3$	8.5 ± 1.0	10.6 ± 1.8	$1.2 \pm .3$		$2.4 \pm .1$
-46	$5.5 \pm .3$	12.7 ± 1.0	11.1 ± 1.8	$0.0 \pm .3$		$2.2 \pm .1$
-74	$6.5 \pm .3$	12.3 ± 1.0	10.1 ± 1.8	$0.0 \pm .3$		$2.1 \pm .1$
-79	$7.8 \pm .3$	$14.0 \pm .4$	$6.3 \pm .3$	0.0	32.0 ± 2.4	$1.2 \pm .05$
-91	$7.7 \pm .3$	13.7 ± 1.0	10.4 ± 1.8			(1.2)

Table 3

ACTIVE NITROGEN BUBBLED THROUGH SOLUTIONS OF SCAVENGERS IN NEAT LIQUID MeOH AT -79°C

[Scavenger]	$10^2 \times \text{Moles of Product/g. Atom of N}$				$N(^4S)$
<u>M</u>	$(CH_2OH)_2$	CH_2O	HCN	H_2	$\mu\text{mole/sec.}$
None	$7.8 \pm .3$	$14.0 \pm .4$	$6.3 \pm .3$	32.0 ± 2.4	1.2
$FeCl_3, .0003$	$2.8 \pm .1$	$18.6 \pm .2$	6.6	19.4 ± 2.0	1.3
$FeCl_3, .0010$	$3.1 \pm .4$	$18.0 \pm .8$	6.8	18.2 ± 4.0	$(1.2)^a$
$FeCl_3, .010$	$3.5 \pm .4$	$18.5 \pm .4$	6.7	$10.4 \pm .4$	$(1.2)^a$
$FeCl_3, .10$	$3.3 \pm .3$	$17.1 \pm .3$	6.8	$7.1 \pm .1$	$(1.2)^a$
$FeCl_3, .675$	3.4			6.4	$(1.2)^a$
$MyCl_2, .0010$	9.1	13.6			1.2
$FeSO_4, .010$		$14.7 \pm .5$		33.0 ± 1.7	1.2

a. Assumed.

Table 4

ACTIVE NITROGEN IMPINGED ON NEAT LIQUID MeOH

Temp °C	Scavenger M	10 ² x Moles of Product/g. Atom N				N(⁴ S) μmole/sec
		(CH ₂ OH) ₂	CH ₂ O	HCN	H ₂	
-79	None	8.3 ± .4	13.5 ± .4	11.1 ± .4	30.0	(1.2) ^a
-79	FeCl ₃ , .0010	7.5 ± 1.0	11.1 ± 1.0	10.1 ± .3	26.4	1.3
-79	FeCl ₃ , .005	8.3 ± .1	12.7 ± .8	9.8 ± .9		(1.2) ^a
-79	FeCl ₃ , .010	6.8 ± .3	12.6 ± .6	10.3 ± .1	28.1	(1.2) ^a
-91	None	5.9	12.3	8.5		1.2 ^a
-94	None	5.1	9.6	12.3		(1.2) ^a

a. Assumed

Table 5

ACTIVE NITROGEN WITH METHANOL VAPOR AT ROOM TEMPERATURE

Total Pressure Torr	10 ² x Moles of Product/g. Atom N			MeOH μmole/sec	N(⁴ S)
	(CH ₂ OH) ₂	CH ₂ O	HCN		
2.0	0.6	0.5	1.2	.93	1.3
8.5	1.5	1.2	3.9	.97	1.3

Table 6

ACTIVE NITROGEN PREMIXED WITH METHANOL VAPOR REACTING WITH NEAT LIQUIDS

Total Pressure Torr	Liquid	Temp °C	10 ² x Moles of Product/g. Atom N				MeOH μmole/sec	N(⁴ S)
			(CH ₂ OH) ₂	CH ₂ O	HCN	NH ₃		
10	H ₂ O	~25	4.6	1.4	12.5	3.2	3.1	2.5
10	MeOH	-10	3.0	7.0	17.0	0.4	.8	2.2
7	MeOH	-79	10.0	10.4	10.9	0.0	.9	2.1

Table 7

ACTIVE NITROGEN WITH LIQUID AQUEOUS ETHANOL AT $5 \pm 3^\circ\text{C}$

<u>[EtOH]</u>	<u>10^2 x Moles of Product/g. Atom EtOH</u>			<u>N(^4S)</u>
<u>M</u>	<u>CH₃CHO</u>	<u>HCN</u>	<u>NH₃</u>	<u>$\mu\text{mole/sec}$</u>
2	1.3 $\pm$.2	17.0 $\pm$ 2.5	3.4 $\pm$ 1.1	1.2 $\pm$.1
5	.8 $\pm$.1	18.7 $\pm$ 2.1	3.7 $\pm$ 1.1	1.3 $\pm$.2
10		25.8		1.5
11		21.0		1.0
13		30.0		1.0
15		32.0		1.0
17	1.3	9.5	3.9	(1.2) ^a

a. Assumed

Table 8

ACTIVE NITROGEN WITH NEAT LIQUID ETHANOL AT -79°C

Scavenger	10 ² x Moles of Product/g. Atom N					N(⁴ S) μmole/sec
	(CH ₃ CHOH) ₂	(CH ₂ CH ₂ OH) ₂	CH ₃ CHOHCH ₂ OH	CH ₃ CHO	CH ₂ O	HCN
BUBBLED THROUGH						
None	6.0 ± .5	.14 ± .05	.8 ± .1	1.9 ± .1	1.3 ± .2	25.3 ± 1.0
FeCl ₃ .001	.3 ± .1	.01 ± .01	.1 ± .1	2.9	1.8 ± .2	27.9
						(1.2) ^a (1.2) ^a
IMPINGED						
None	1.1 ± .3	.2 ± .1	.2 ± .1	.5 ± .2	.4 ± .1	6.4 ± .4
FeCl ₃ .001	1.0 ± .2	.3 ± .1	.2 ± .1	1.0 ± .2	.9 ± .4	7.6 ± .7
						(1.2) ^a (1.2) ^a

a. Assumed

V. BIBLIOGRAPHY OF PUBLICATIONS

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5. V. Franchetti-Sicignano, "Surface Decomposition of Liquid Methanol and Ethanol by Active Nitrogen", Ph.D. dissertation, Boston University Graduate School, 1976.

VI. PARTICIPATING PERSONNEL

1. Norman N. Lichtin, Ph.D., Principal Investigator.
2. Victoria Franchetti-Sicignano, Research Assistant, received Ph.D. in 1976 on basis of this research.
3. Jon M. Brooks, Ph.D., part time Research Associate.
4. Stephen E. Jukins, Ph.D., part time Research Associate.
5. Drora Levy, Ph.D., part time Research Associate.

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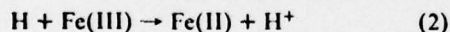
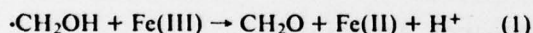
The Basis for Chemical Attack by Active Nitrogen on Liquid Methanol. Induction of Molecular Decomposition by Recombination Events

Sir:

Although $(\text{CH}_2\text{OH})_2$ and CH_2O are, in addition to HCN, the only organic compounds formed in significant yield by the reaction at 9°C of "active nitrogen" with aqueous methanol,¹ neither the ratio of their yields² ($(\text{CH}_2\text{OH})_2/\text{CH}_2\text{O} = 0.25$) nor the large increase in production of $(\text{CH}_2\text{OH})_2$ when tetranitromethane is used as a scavenger³ is consistent with their formation via combination and disproportionation of free $\cdot\text{CH}_2\text{OH}$ radical. We now report results of an investigation of the reaction of "active nitrogen" with neat liquid methanol at -79° . These results show that $\cdot\text{CH}_2\text{OH}$ radicals and H atoms are formed but that free radicals homogeneously distributed in bulk solution are precursors of only a minor portion of the observed stable products. It is proposed that chemical changes are initiated by decomposition of methanol molecules by deposition of energy of recombination of nitrogen atoms; part of the products are produced by direct dissociation to stable molecules, part via the intermediacy of free radicals.

"Active nitrogen" was produced in a fast-flow, low vacuum system⁴ by irradiation with 2450-MHz microwaves. The flow rate of $\text{N}(\text{S})$ was determined by NO titration.⁵ The reaction flask was cooled by a Dry Ice-acetone bath and the solution temperature was measured during reaction by means of a thermocouple. Yields of HCN,⁶ CH_2O ,⁷ and $(\text{CH}_2\text{OH})_2$ ⁸ were determined by standard methods. H_2 was sampled by Toepler pumping and analyzed by mass spectrometry or gas chromatography. Phenyl-*tert*-butyl nitron (PBN) was used to trap free radicals and identify them by EPR.⁹

$\cdot\text{CH}_2\text{OH}$ and H atom were the only radicals detected by spin trapping (see below). This technique cannot give quantitative data because trapping efficiencies are not known. The radicals were monitored conveniently by means of their reactions with $\text{Fe}(\text{III})$.¹⁰

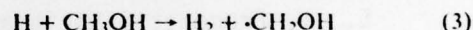


The isotopic composition of molecular hydrogen from CH_3OD was used as a probe of precursors of CH_2O and glycol.

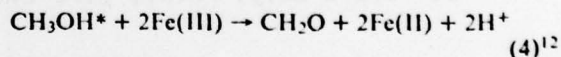
The only detectable products of the reaction with neat CH_3OH were $(\text{CH}_2\text{OH})_2$, CH_2O , HCN, and H_2 . (See Table I for yields in the absence and presence of FeCl_3 .) Yields were not affected significantly by 0.001 M MgCl_2 .

Molecular hydrogen obtained with CH_3OD as substrate did not contain a significant amount of D_2 and was composed of approximately equal amounts of HD and H_2 . The only significant components of the EPR spin adduct spectrum were a triplet of triplets, $a_N = 15.7$ and $a_H = 8.4$ g, and a triplet of doublets, $a_N = 15.2$ and $a_H = 3.6$ g. These can be assigned respectively to the adducts of H atom¹¹ and $\cdot\text{CH}_2\text{OH}$ or $\cdot\text{CH}_3$.¹¹ $\cdot\text{CH}_3$ can be excluded as a significant intermediate because CH_4 could not be detected in the gaseous products by either gas chromatography or mass spectrometry.

Ferric chloride has little, if any, effect on the yield of HCN; $3 \times 10^{-4}\text{ M}$ FeCl_3 alters the yield of $(\text{CH}_2\text{OH})_2$ and CH_2O by amounts which are not changed on increasing the concentration of scavenger up to $1 \times 10^{-1}\text{ M}$. In contrast, the yield of H_2 is affected equally by 3×10^{-4} and $1 \times 10^{-3}\text{ M}$ scavenger but is reduced further by $1 \times 10^{-2}\text{ M}$ and somewhat more by $1 \times 10^{-1}\text{ M}$ FeCl_3 . The decrease in yield of H_2 by up to $1 \times 10^{-3}\text{ M}$ FeCl_3 is equal within experimental error to twice the observed decrease in glycol yield. This approximate equality indicates that the precursor of most of the *scavengeable* glycol is $\cdot\text{CH}_2\text{OH}$ radical formed in bulk solution by reaction 3, rather than formed directly by action of N atoms upon CH_3OH .



Apparently, even at the lowest concentration of FeCl_3 used, all H atoms which diffuse into bulk solution are scavenged. It can be further noted that if free homogeneously distributed $\cdot\text{CH}_2\text{OH}$ were the precursor of $(\text{CH}_2\text{OH})_2$ and CH_2O , reaction 1 would suppress $(\text{CH}_2\text{OH})_2$ completely and increase the yield of CH_2O by an amount equal to twice the yield of glycol plus the yield of CH_2O in the absence of scavenger, i.e., by 27.5 ± 1 in the units of Table I. The observed small increase in yield of CH_2O in the presence of $0.0003\text{--}0.1\text{ M}$ FeCl_3 , 3.7 ± 0.6 , apparently reflects a minor yield (i.e., 3.7) of free $\cdot\text{CH}_2\text{OH}$. The observed large yield of HD from CH_3OD is also not consistent with formation of all or most of the glycol and CH_2O by combination and disproportionation of $\cdot\text{CH}_2\text{OH}$. It is consistent with unimolecular dissociation of a highly energetic CH_3OD molecule to give CH_2O and HD. Reduction of yields of H_2 , but not of CH_2O , by high concentrations of FeCl_3 can be explained by reaction 4.



Presumably, unscavengeable glycol results from a bimolec-

Table I. Product Yields^{a, b}

$(\text{FeCl}_3), \text{M}$	$(10^3 \times \text{moles of product}^c)/(\text{g atoms of incident N})$			
	$(\text{CH}_2\text{OH})_2$	CH_2O	HCN	H_2
0	7.0 ± 0.4 (10)	13.5 ± 0.5 (10)	5.6 ± 0.4 (10)	28.7 ± 1.5 (4)
3×10^{-4}	2.6 ± 0.1 (2)	17.2 ± 0.3 (2)	6.4 (1)	18.0 ± 1.5 (2)
1×10^{-3}	2.5 ± 0.2 (2)	17.2 ± 1.5 (2)	6.2 (1)	18.3 ± 2 (3)
1×10^{-2}	2.9 ± 0.5 (2)	17.0 ± 1.4 (2)	6.4 (1)	9.6 ± 1 (2)
1×10^{-1}	2.9 ± 0.2 (2)	17.3 ± 1.2 (2)	6.3 (1)	6.5 ± 1 (2)

^a Flow rate of atomic nitrogen $1.3 \times 10^{-6}\text{ mol sec}^{-1}$. ^b Indicated uncertainties are standard deviations. ^c Numbers in parentheses indicate numbers of complete replicate experiments. Analyses were performed in triplicate for every replicate experiment.

ular process involving one or two CH_3OH^* molecules which is not intercepted even by 0.1 M FeCl_3 .

Generation of CH_3OH^* can be ascribed to energy released by recombination of $\text{N}(^4\text{S})$ atoms, a process which in the gas phase proceeds largely via $\text{N}_2(\text{A}^3\Sigma_u^+)$.¹³ Methanol is known to quench the latter species in the gas phase.¹⁴ Analogous gas phase quenching of $\text{N}_2(\text{A}^3\Sigma_u^+)$ leads to the decomposition of H_2 ,^{15,16} CO_2 ,¹⁶ N_2O ,¹⁶ and NH_3 .¹⁷ The total energy released on recombination of nitrogen atoms is 225 kcal/mol. Either this energy or the 142 kcal/mol of the 0 vibrational level of $\text{N}_2(\text{A}^3\Sigma_u^+)$ is more than sufficient to bring about the decomposition of the methanol molecule. We wish to suggest that energy released on recombination of nitrogen atoms induces decomposition of methanol in localized regions not unlike the "spur" regions which are well known in radiolysis of water.¹⁸ Spin selection rules and energetic considerations respectively militate against insertion and abstraction reactions of nitrogen atom. Its reactions with saturated substrates in condensed phase are apparently governed by the process described above. This chemistry is unusual, and perhaps unique, among atomic reagents.

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