k_3'(CO) down to that of **3** at the same CO concentration is 0.11 *M* compared to 10^{-5} *M* present in the usual solutions of **3**. This means that aggregation through imidazole–iron bonding is no problem below about 0.01 *M* in **1** or **2**.

(21) F. S. Mathews and P. Strittmatter, *J. Mol. Biol.*, **41**, 295 (1969).

(22) NOTE ADDED IN PROOF. Titration of an aqueous suspension of **2** with acid brings about an isosbestic change of the Soret band from that of five-coordinate[4a] to that of four-coordinate (or aquo) heme[13] with a half point at pH 3.6, in agreement with the kinetic results.

J. Geibel, C. K. Chang, T. G. Traylor*
Department of Chemistry, University of California, San Diego
La Jolla, California 92093

Received May 5, 1975

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

Sir:

Although $(CH_2OH)_2$ 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 yields[2] ($(CH_2OH)_2/CH_2O = 0.25$) nor the large increase in production of $(CH_2OH)_2$ when tetranitromethane is used as a scavenger[3] is consistent with their formation via combination and disproportionation of free $\cdot CH_2OH$ radical. We now report results of an investigation of the reaction of "active nitrogen" with neat liquid methanol at −79°. These results show that $\cdot CH_2OH$ 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 system[4] by irradiation with 2450-MHz microwaves. The flow rate of $N(^4S)$ 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 $(CH_2OH)_2$[8] were determined by standard methods. H_2 was sampled by Toepler pumping and analyzed by mass spectrometry or gas chromatography. Phenyl-*tert*-butyl nitrone (PBN) was used to trap free radicals and identify them by EPR.[9]

$\cdot CH_2OH$ 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 Fe(III).[10]

$$\cdot CH_2OH + Fe(III) \rightarrow CH_2O + Fe(II) + H^+ \qquad (1)$$

$$H + Fe(III) \rightarrow Fe(II) + H^+ \qquad (2)$$

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 $(CH_2OH)_2$, 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 atom[11] and $\cdot CH_2OH$ or $\cdot CH_3$.[11] $\cdot CH_3$ 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; 3×10^{-4} *M* $FeCl_3$ alters the yield of $(CH_2OH)_2$ and CH_2O by amounts which are not changed on increasing the concentration of scavenger up to 1×10^{-1} *M*. In contrast, the yield of H_2 is affected equally by 3×10^{-4} and 1×10^{-3} *M* scavenger but is reduced further by 1×10^{-2} *M* and somewhat more by 1×10^{-1} *M* $FeCl_3$. The decrease in yield of H_2 by up to 1×10^{-3} *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 $\cdot CH_2OH$ radical formed in bulk solution by reaction 3, rather than formed directly by action of N atoms upon CH_3OH.

$$H + CH_3OH \rightarrow H_2 + \cdot CH_2OH \qquad (3)$$

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 $\cdot CH_2OH$ were the precursor of $(CH_2OH)_2$ and CH_2O, reaction 1 would suppress $(CH_2OH)_2$ 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 0.0003–0.1 *M* $FeCl_3$, 3.7 ± 0.6, apparently reflects a minor yield (i.e., 3.7) of free $\cdot CH_2OH$. 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 $\cdot CH_2OD$. 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.

$$CH_3OH^* + 2Fe(III) \rightarrow CH_2O + 2Fe(II) + 2H^+ \qquad (4)^{12}$$

Presumably, unscavengeable glycol results from a bimolec-

Table I. Product Yields[a,b]

$(FeCl_3)$, *M*	$(10^2 \times$ moles of product[c])/(g atoms of incident N) $(CH_2OH)_2$	 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 1.3×10^{-6} 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 $N(^4S)$ atoms, a process which in the gas phase proceeds largely via $N_2(A^3\Sigma_u^+)$.[13] Methanol is known to quench the latter species in the gas phase.[14] Analogous gas phase quenching of $N_2(A^3\Sigma_u^+)$ 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 $N_2(A^3\Sigma_u^+)$ 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.

Acknowledgment. This research was supported by the U.S. Army Research Office—Durham under Grant No. DA-ARO-D-31-124-72-G195 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) C. T. Chen and N. N. Lichtin, *J. Am. Chem. Soc.*, **92**, 7506 (1970).

(2) The recombination:disproportionation ratio for $\cdot CH_2OH$ in aqueous solution is reported to be 6 to 12: U. Sokolov and G. Stein, *J. Chem. Phys.*, **44**, 3329 (1966); R. Seki, R. Nagai, and M. Immamura, *Bull. Chem. Soc. Jpn.*, **41**, 2877 (1968).

(3) $k(\cdot CH_2OH + TNM)_{aq} = 5 \times 10^9\ M^{-1}\ sec^{-1}$, K. D. Asmus, A. Henglein, M. Ebert, and J. P. Keene, *Ber. Bunsenges. Phys. Chem.*, 657 (1964).

(4) See A. Fujino, S. Lundsted, and N. N. Lichtin, *J. Am. Chem. Soc.*, **88**, 775 (1966), for a description of apparatus. The gas stream was introduced 1–2 cm below the surface of the liquid.

(5) P. Harteck, G. Mannella, and R. R. Reeves, *J. Chem. Phys.*, **29**, 608 (1958).

(6) J. M. Kruse and M. G. Mellon, *Anal. Chem.*, **25**, 446 (1953).

(7) C. E. Brucker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

(8) N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

(9) S. W. Mao and L. Kevan, *J. Phys. Chem.*, **78**, 91 (1974).

(10) G. E. Adams and J. H. Baxendale, *J. Am. Chem. Soc.*, **80**, 4215 (1958).

(11) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, **91**, 4481 (1969).

(12) Even at room temperature $FeCl_3$ is reduced slowly when dissolved in methanol. Necessary small corrections were made in determining yields of CH_2O.

(13) A. N. Wright and C. A. Winkler, "Active Nitrogen", Academic Press, New York, N.Y., 1968, pp 88–113.

(14) J. A. Meyer, D. W. Setser, and W. G. Clark, *J. Phys. Chem.*, **76**, 1 (1972).

(15) V. Vadlamudy and C. I. Winkler, *Can. J. Chem.*, **45**, 2463 (1967).

(16) I. M. Campbell and B. A. Thrush, *Trans. Faraday Soc.*, **64**, 1275 (1968).

(17) H. B. Dunford, *J. Phys. Chem.*, **67**, 258 (1962).

(18) I. G. Draganic and Z. D. Draganic, "The Radiation Chemistry of Water", Academic Press, New York, N.Y., 1971, pp 171–189.

Victoria Franchetti, Jon M. Brooks, Norman N. Lichtin*
Department of Chemistry, Boston University
Boston, Massachusetts 02215

Received May 12, 1975

Oxidation of Alcohols to Aldehydes by Reagents Derived from Chromyl Chloride

Sir:

The Collins oxidation[1] and its modification by Ratcliffe[2] are among[3] the most reliable procedures for the oxidation of a saturated primary alcohol to its corresponding aldehyde. An unfortunate aspect of these chromium trioxide-pyridine based reagents is that about 6 equiv of oxidant are needed to ensure rapid and complete oxidation. It is apparent that this requirement for excess oxidant is due, at least in part, to the production of water during the course of the oxidation (eq 1). Collins had previously shown[1] that reagent **1** reacts rapidly with water to produce the insoluble pyridinium dichromate **3**. The basic chromium dioxide species **2** is also likely to coordinate with, and deactivate, further quantities of reagent **1**. We reasoned that both of these problems might be overcome if chlorine were the hydrogen acceptor rather than oxygen. In support of these arguments we have found that when chromyl chloride (CrO_2Cl_2, **4**) is used in place of chromium trioxide 1.1 equiv of reagent are sufficient to effect complete oxidation.

Table I. Per Cent Yield[a] of Aldehyde or Ketone

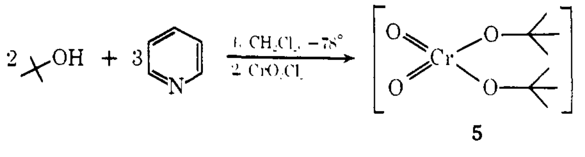
Alcohol	Moles	% CrO_2Cl_2[b]	% **5**[c]
1-Decanol	0.1	—	84
	0.5	—	79
1-Dodecanol	0.01	94	99
Citronellol	0.01	87	93
	0.1	—	84
Geraniol	0.01	87[d]	100[d]
2-Methyl-2-phenyl-propanol	0.1	—	86
Benzyl alcohol	0.01	85	100
Cyclohexane methanol	0.01	90	99
Cyclododecanol	0.01	99	97
Cinnamyl alcohol	0.01	78	86
Pinocarveol	0.01	82	60
3-Hydroxy benzyl alcohol	0.01	0	38

[a] The yields of the small scale reactions (0.01 mol) were determined by GLC relative to an internal standard; all other yields (i.e., 0.1 and 0.5 mol) are for distilled pure substances. [b] These reactions were all carried out on a 10 mmol scale, and the procedure is the same as that described for the use of reagent 5 for oxidation of 1-decanol on a 0.1 mol scale with the exception that *tert*-butyl alcohol was omitted and that 4 rather than 3 equiv of pyridine was used. [c] All these oxidations were carried out exactly as described for the oxidation of 0.1 mol of 1-decanol. However, on the 0.01 mol scale it is not necessary to dilute the CrO_2Cl_2 with CCl_4 prior to addition. [d] Z–E isomerization occurs and one obtains a 3:1 mixture of geranial and neral.

$$\underset{\mathbf{1}}{CrO_3{\cdot}2pyr} + RCH_2OH \rightarrow \underset{\mathbf{2}}{CrO_2{\cdot}2pyr} + RCHO + H_2O \qquad (1)$$

$$\mathbf{1} + H_2O \rightarrow \underset{\mathbf{3}}{Cr_2O_7^{2-}(pyr\,H^+)_2} \qquad (2)$$

When chromyl chloride is added to a solution of pyridine in methylene chloride cooled in a Dry Ice-acetone bath, a red-brown slurry is produced.[4] The alcohol is added to this slurry and rapid oxidation ensues even at −70°. The reaction mixture is allowed to warm to ambient temperature and good to excellent yields of aldehydes are realized (see Table I under CrO_2Cl_2). Unfortunately, this oxidation is so vigorous that it is difficult to control on a scale much larger than 10 mmol. In order to overcome this problem the reagent was modified further by addition of *tert*-butyl alcohol (eq 3). The reagent (**5**) thus produced is remarkably effective for these oxidations on both small and large scales (see Table I under reagent **5**). Since reagent **5** is probably di-*tert*-butyl chromate, or its pyridine adduct, one might as-



(3)

5