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Alkyldiazenes. Gas-Phase and Solution Chemistry. Physical and Chemical Properties of Methyldiazene

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A series of monosubstituted alkyldiazenes, $RN{=}NH$ ($R = CH_3$, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, and $(CH_3)_3C$), were synthesized from the reaction of the appropriate *N*-alkylhydroxylamine with hydroxylamine-*O*-sulfonate ion in aqueous alkaline solution. Studies in aqueous solution include ultraviolet–visible absorption data (λ_{max}, ϵ) and stoichiometries of decomposition under acid and alkaline conditions. In alkaline solution the products are nitrogen, hydrazine, an alkane, and an aldehyde or ketone. The rapid decomposition in acid solution produces a variety of products which are interpreted as arising *via* the intermediate formation of the alkylcarbonium ion, R^+, and the parent diazene, $HN{=}NH$. Physical and chemical properties of methyldiazene were investigated using both $CH_3N{=}NH$ and the kinetically more stable isomer $CH_3N{=}ND$. Pure methyldiazene has a melting point of $-122 \pm 1°$ while vapor pressure measurements give a boiling point of $-2 \pm 5°$ with $\Delta H_v° = 7140 \pm 350$ cal mol^{-1} and $\Delta S_v° = 26.3 \pm 1.8$ eu. Comparison with data from similar measurements on azomethane, $CH_3N{=}NCH_3$ (bp $-1.5°$, $\Delta H_v° = 1650 \pm 150$ cal mol^{-1}, $\Delta S_v° = 22.4 \pm 0.5$ eu), suggests that liquid methyldiazene is substantially hydrogen bonded. In the gas phase the decomposition of methyldiazene follows the rate law $dP/dt = -k_{obsd}P^{3/2}$ where P is the pressure of the diazene. At $23 \pm 1°$ k_{obsd} equals 0.93 ± 0.08 and 0.11 ± 0.01 $M^{-1/2}$ sec^{-1} for $CH_3N{=}NH$ and $CH_3N{=}ND$, respectively. A radical chain mechanism is proposed. Gaseous methyldiazene reacts violently with oxygen. Finally the distinctive features generally characteristic of the gas-phase vibrational spectra of monosubstituted alkyldiazenes are described based upon the examination of the gas-phase infrared spectra of $CH_3N{=}NH$, $CH_3N{=}ND$, $CD_3N{=}NH$, $CD_3N{=}ND$, $CH_3CH_2N{=}NH$, and $CH_3CH_2N{=}ND$.

Monosubstituted diazenes, $RN{=}NH$, have been postulated as intermediates in many reactions, but only recently have such molecules been synthesized and a study of their chemistry begun.[1] The properties and reactions of these compounds can be expected to reflect largely the chemistry of their novel $N{=}N{-}H$ moiety. Methyldiazene, $CH_3N{=}NH$, is of particular interest since it is both the simplest monosubstituted diazene yet made and it is the only molecule of this class that can be readily isolated as a pure material. This paper describes the properties of methyldiazene with primary emphasis on its aqueous solution and gas-phase chemistry. Some chemistry of the ethyl, *n*-propyl, isopropyl, and *tert*-butyl homologs is also included.[2]

Experimental Section

General.—Spectra were recorded with the following instruments: Ultraviolet–visible with a Cary 17 spectrometer, a Bausch and Lomb 505 spectrometer, and a Beckman DU spectrometer modified by Gilford Instruments; mass spectra with a Perkin-Elmer RMS-4 mass spectrometer; nmr with a Varian A-60 spectrometer; infrared with a Perkin-Elmer 621 spectrometer. A 10-cm cell with KBr or CsI windows was used for gas-phase infrared spectra. Nitrogen and hydrocarbon analyses were performed by gas chromatography using a silica gel column with hydrogen carrier gas at 40°.[3] Unless otherwise stated all chemicals were reagent grade and used without further purification. Melting points cited are uncorrected.

Preparation of Compounds.—Hydroxylamine-*O*-sulfonic acid (HOS) was prepared as previously described.[4]

N-Alkylhydroxylamines were obtained as the oxalate salts by hydrogenation of the corresponding alkylnitro compound on 5% palladium on barium sulfate (Matheson, Coleman and Bell) at atmospheric pressure in the presence of a stoichiometric amount of oxalic acid.[5] Attempts to speed up the reduction by raising the pressure of hydrogen above 1 atm caused formation of the alkylamine. Yields ranged from 50 to 70% of there crystallized salts using 0.1–0.2 mol of the nitro compound. In the *tert*-butyl case the reduction proceeded more slowly with a yield of ~25%. Physical data for the salts $(RNH_2OH)_2C_2O_4$ are summarized in Table I.

TABLE I
PHYSICAL DATA OF *N*-ALKYLHYDROXYLAMMONIUM OXALATE SALTS

R	Mp, °C Found	Lit.	Ref	Neut equiv Found	Calcd
Methyl	158–160	158	4	93.3	92.1
Ethyl	104–106	107–108	*a*	109.7	106.1
n-Propyl	153–155	154–155	*b*	120.8	120.1
Isopropyl	157–159	157–160	*b*	121.6	120.1
tert-Butyl	203–205	200–202	*c*	134.2	134.1

[a] P. E. Iverson and H. Lund, *Acta Chem. Scand.*, **19**, 2303 (1965). [b] A. I. Ryer and G. B. L. Smith, *J. Amer. Chem. Soc.*, **73**, 5675 (1951). [c] P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *ibid.*, **86**, 1139 (1964).

N-Methylhydroxylammonium-*methyl*-d_3 was synthesized similarly from nitromethane-d_3 (Diaprep, Inc., 99+%).

Azomethane[6] and *trans*-chlorohydridobis(triethylphosphine)platinum(II)[7] were prepared by literature methods.

Synthesis of Alkyldiazenes.—A solution of a desired alkyldiazene was readily obtained by adding an aqueous hydroxide solution of an *N*-alkylhydroxylammonium oxalate salt to HOS either as a solid or in solution. In the reaction solution the concentrations were typically 0.01–0.1 *M* HOS, 0.02–0.3 *M* *N*-alkylhydroxylamine, and 0.1–2.0 *M* NaOH or KOH. Under these conditions diazene generation is complete in 1–5 min; the rate law shows a first-order dependence on HOS, alkylhydroxylamine, and hydroxide ion.[8]

N-Deuteriodiazenes were generated using a sodium deuterioxide solution prepared by adding sodium to D_2O (Diaprep, Inc., 99.8%).

Methyl- and ethyldiazenes and their *N*-deuterio isomers were isolated from their solutions as pure compounds as previously described.[4] Yields of pure $CH_3N{=}NH$ and $CH_3N{=}ND$ are typically 30–40 and 50–60%, respectively using 25 ml of 2 *M* NaOH (NaOD), 3–5 mmol of HOS, and a twofold excess of *N*-methylhydroxylamine.

Extinction Coefficients.—Alkyldiazene was generated by rapid addition of an HOS solution to a solution of KOH and a molar excess of the *N*-alkylhydroxylammonium oxalate salt. After

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(1) For a recent review see E. M. Kosower, *Accounts Chem. Res.*, **4**, 193 (1971).

(2) A preliminary account of some of this work has appeared. M. N. Ackermann, J. L. Ellenson, and D. H. Robison, *J. Amer. Chem. Soc.*, **90**, 7173 (1968).

(3) N. Brenner, *Anal. Chem.*, **31**, 1815 (1959).

(4) M. N. Ackermann, *Inorg. Chem.*, **10**, 272 (1971).

(5) E. Schmidt, A. Ascherl, and L. Mayer, *Ber.*, **58**, 2430 (1925).

(6) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(7) G. W. Parshall, *Inorg. Syn.*, **12**, 26 (1970).

(8) P. L. Matlock and M. N. Ackermann, unpublished results.

thorough mixing the optical density (OD) of the solution at λ_{max} was recorded as a function of time. The OD rapidly increased to a maximum and then gradually decreased. The molar extinction coefficient, ϵ, was calculated by assuming that the maximum OD corresponded to a diazene concentration equal to that of HOS. Various combinations of hydroxide, HOS, and *N*-alkylhydroxylamine concentrations were tried to maximize the value of ϵ. Concentration ranges used were 0.4–1.5, 0.01–0.02, and 0.1–0.2 *M*, respectively. The final solution was also made $\sim 10^{-3}$ *M* in ethylenediaminetetraacetate ion to prevent possible catalytic decomposition of the diazene by traces of heavy-metal ions. In general larger ϵ values were obtained in those runs in which OD_{max} was reached in the shortest time. The best value of ϵ was taken to be that which could not be increased by increasing the hydroxide and/or hydroxylamine concentrations at a fixed HOS concentration.

The same procedure was employed in the determination of ϵ under anaerobic conditions to check on the influence of oxygen. Standard syringe techniques were employed, and the nitrogen used was scrubbed free of traces of oxygen by forcing it through two stages of fine fritted-glass tubes immersed in acidic chromous solutions over amalgamated zinc.[9] Solutions were prepared from deoxygenated water and stored under a positive pressure of nitrogen. Syringes were flushed with nitrogen before use. The diazene was generated in a silica cuvet fitted with a small vent in the serum cap to allow the gases formed to escape.

Stoichiometry of Alkaline Decomposition of Alkyldiazenes.—An aqueous alkaline solution of the diazene was generated in a vacuum system by addition of a degassed NaOH solution of the *N*-alkylhydroxylamine to solid HOS. When diazene decomposition was complete the gaseous products were measured and analyzed by infrared spectrometry and gas chromatography.[3] The solution was analyzed spectrophotometrically for hydrazine[10] and gravimetrically for aldehyde or ketone.[11] Trials of known mixtures demonstrated that the other substances present did not interfere with the analysis being performed. The alkaline decomposition of *N*-alkylhydroxylamines is too slow to affect these studies.

Reaction of Methyldiazene with Acid.—One to two millimoles of $CH_3N{=}NH$ or $CH_3N{=}ND$ was condensed at −196° into a small flask on a vacuum line, 10 ml of an H_2SO_4, D_2SO_4, or HCl solution was added, and the mixture brought quickly to room temperature. The reaction was accompanied by gas evolution and appeared to be complete in the time of mixing. Analyses for N_2, CH_4, CH_3D, and CH_3Cl (HCl solution) were performed by infrared and mass spectrometry and gas chromatography. The nmr spectrum of the aqueous phase revealed three (in HCl) or four (in H_2SO_4 or D_2SO_4) singlets which were identified as methylhydrazine (δ 2.99),[12] 1,1-dimethylhydrazine (δ 3.15), methanol (δ 3.43), and methyl sulfate (δ 3.81) by showing coincident nmr signals with known compounds added to the sample. The concentration of each component was obtained by adding a known weight ($\sim$6 mg) of tetramethylammonium bromide (δ 3.28) to 1.0 ml of the solution and comparing nmr peak areas. The sum of the hydrazine, methylhydrazine, and 1,1-dimethylhydrazine content was determined spectrophotometrically at 460 nm by the *p*-*N*,*N*-dimethylaminobenzaldehyde method using ϵ values obtained from standard solutions.[10] Hydrazine was determined by difference using the nmr data. Iodometric titration of total hydrazine[13] confirmed the combined nmr–spectrophotometric analyses. Removal of most of the water from one aqueous portion followed by several washings with an absolute ether–absolute ethanol mixture yielded a white solid whose melting point (137–142°) and infrared spectrum (KBr pellet) agreed closely with the melting point (139–141°) and infrared spectrum of an authentic sample of methylhydrazinium hydrogen sulfate, $(CH_3NHNH_3^+)(HSO_4^-)$.

Reaction of *n*-Propyldiazene with Acid.—*n*-Propyldiazene was generated in solution on a vacuum line as described in the stoichiometry studies in base (*vide supra*). After diazene production was complete (as determined from a trial run monitored spectrophotometrically), sulfuric acid was added so that the final concentration after neutralization of base was 0.9 *M*. When reaction was complete, the gases were collected and analyzed qualitatively by infrared spectroscopy.

Exchange Studies.—Pure $CH_3N{=}NH$ was isolated at −196° in a flask on a vacuum line. By means of a standard taper arrangement a buffered deuterium oxide solution was added to the diazene and the system quickly brought to room temperature. Gaseous products were collected at times ranging from a few minutes to several hours after mixing and their infrared spectra recorded. The following solutions were employed: 0.1 *M* NaOD, pH *ca.* 7 (sodium phosphate buffer); pH *ca.* 4.5 (sodium acetate buffer), and 0.01 *M* and 1.0 *M* D_2SO_4.

Reaction of Gaseous Methyldiazene with Oxygen.—$CH_3N{=}NH$ or $CH_3N{=}ND$ was condensed in an evacuated flask at −196°. Gaseous oxygen in a twofold molar excess was added and the flask brought to room temperature quickly in a water bath. The reaction was over in the time of warming as indicated by a constant sample pressure. The $CH_3N{=}NH$ reaction was explosive, emitting light and occasionally destroying the flask; the $CH_3N{=}ND$ reaction did not show this violence.

Melting and Boiling Points of $CH_3N{=}ND$.—The melting point was determined by the Stock method[14] after purification of the diazene by several bulb-to-bulb distillations on a vacuum line.

The boiling point of $CH_3N{=}ND$ was estimated from measurements of its vapor pressure at several temperatures. *trans*-Chlorohydridobis(triethylphosphine)platinum(II) was placed at the bottom of a long narrow tube on a vacuum line and the diazene condensed on top of it at −196°. After residual gases were pumped off, a slush bath was placed around the tube and the pressure of the gas above the liquid diazene was measured with a mercury manometer. In each case the pressure either stabilized at a fixed value or gave a nearly constant initial value for several minutes before rising slowly. Several measurements were made at each temperature. Between successive determinations the gases above the sample were removed either by quickly pumping on the sample at the slush bath temperature, or by refreezing the diazene before pumping. About 2 mmol of diazene was used with 1–40 mg of the platinum compound. Little of the platinum compound actually dissolves in the diazene. No stable vapor pressure reading was obtainable in the absence of the platinum compound. Vapor pressures were the following (°C (Torr)): −78 (4.8–5.2), −64 (17–19), −46 (58–65), −37 (100–110).

Vapor Pressure of Azomethane.—The pressure of the gas above a sample of liquid azomethane in a slush bath was read from a mercury manometer. Vapor pressures were the following (°C (Torr)): −78 (solid), −64 (24), −46 (78.5), −37 (127).

Kinetics of Gas-Phase Methyldiazene Decomposition.—Pure $CH_3N{=}NH$ or $CH_3N{=}ND$ was condensed at −196° in a flask fitted with a stopcock, warmed quickly to room temperature in a water bath, shaken with the aid of glass beads to mix the contents, and then connected to a vacuum line. The total pressure was read from a mercury manometer as a function of time until the pressure reached a constant value.

Results and Discussion

Generation of Diazenes and Their Decomposition in Alkaline Solution.—The reaction of hydroxylamine-*O*-sulfonate ion (HOS) with an excess of an *N*-alkylhydroxylamine in alkaline aqueous solution produces the corresponding monosubstituted *N*-alkyldiazene (eq 1). This method has been used for the *N*-alkyl substituents methyl-, ethyl-, propyl-, isopropyl-, and *tert*-butyl-. The reaction proceeds rapidly at room temperature at hydroxide concentrations as low as 0.1 *M;* the rate of generation increases with increases in hydroxide concentration.

$$H_2NOSO_3^- + RNHOH + OH^- \longrightarrow RN{=}NH + SO_4^{2-} + 2H_2O \quad (1)$$

The quantitative formation of diazenes according to eq 1 is deduced from stoichiometry studies in which HOS is the limiting reagent. When the synthesis of diazenes was carried out on a vacuum line and the

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[9] R. E. Dodd and P. L. Robinson, "Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1957, p 167.

[10] G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, **84**, 1797 (1962).

[11] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd ed, Wiley, New York, N. Y., 1963, p 91.

[12] All δ values are quoted relative to external TMS, 1% in $CDCl_3$.

[13] Reference 11, p 537.

[14] Reference 9, p 331.

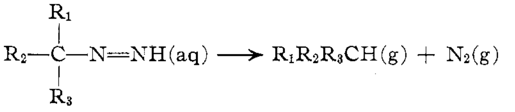
TABLE II

STOICHIOMETRIC RESULTS OF DECOMPOSITION OF ALKYLDIAZENES IN ALKALINE SOLUTION

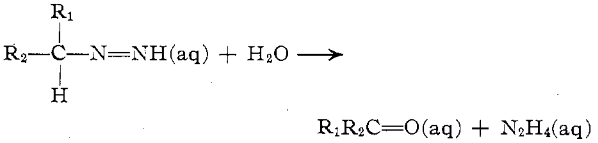
				N_2H_4		N_2		$RCH{=}O$ or $R_1R_2C{=}O$		RH			
Alkyldiazene	$[OH^-]$, *M*	$H_3N^+OSO_3^-$, mmol	RNHOH, mmol	mmol	% total N	mmol	% total N	mmol	% total C	mmol	% total C	(Total N recovered, mmol)/2	Total C recovered, mmol
Methyl	0.36	3.53	6.85	1.94	54	1.63	46	1.28	44	1.63	56	3.57	2.91
Methyl	0.18	3.00	6.00	1.70	57	1.28	43	*b*		1.20		2.98	
Methyl	0.36	*a*	*a*	0.24	13	1.62	87	0.23	13	1.62	87	1.86	1.85
Ethyl	0.36	3.64	6.56	0.52	14	3.12	86	0.59	16	3.11	84	3.64	3.70
n-Propyl	0.39	3.51	6.05	0.92	25	2.70	75	1.04	28	2.70	72	3.62	3.74
Isopropyl	0.32	1.00	3.0	0.16	19	0.70	81	*b*		0.66		0.86	
Isopropyl	0.39	3.65	6.63	0.05	1	3.33	99	0	0	3.33	100	3.38	3.33
tert-Butyl	0.37	1.23	1.28	0	0	0.84	100	0	0	0.80	100	0.84	0.80

[a] Methyldiazene added as pure substance. Amount not measurable. [b] Not measured.

diazenes allowed to fully decompose, the products were an alkane, nitrogen, hydrazine, and an aldehyde or ketone. The stoichiometric data are summarized in Table II. Assuming diazene production according to eq 1, the products found generally account for at least 90% of the diazene produced. The low product yield in the *tert*-butyl case is attributed to partial hydrolysis of the HOS under conditions where hydroxylamine is not present in excess. The products of diazene decomposition are explicable in terms of eq 2 and 3. The



$$R_2\text{—}C(R_1)(R_3)\text{—}N{=}NH(aq) \longrightarrow R_1R_2R_3CH(g) + N_2(g) \qquad (2)$$



$$R_2\text{—}C(R_1)(H)\text{—}N{=}NH(aq) + H_2O \longrightarrow R_1R_2C{=}O(aq) + N_2H_4(aq) \qquad (3)$$

aldehyde or ketone and hydrazine probably arise from rearrangement of the alkyldiazene to the hydrazone followed by hydrolysis in a manner similar to that established for azomethane (1,2-dimethyldiazene).[15] As expected the hydrazone pathway assumes less importance as the number of α-hydrogen atoms decreases, and none is formed from the *tert*-butyldiazene.

The nature of the products of alkyldiazene decomposition in alkaline solution are not affected by the excess *N*-alkylhydroxylamine present in the generating solution. This is demonstrated by entry three in Table II which gives the results of adding a sodium hydroxide solution to pure methyldiazene. The only detectable products in this run agree with the other stoichiometric data. The higher proportion of gaseous products may be due to partial vaporization of the methyldiazene.

Absorption Data.—The rapid quantitative generation of alkyldiazenes, *in situ*, on a time scale during which decomposition was negligible yielded the absorption data in Table III. All solutions contained sodium hydroxide and alkylhydroxylammonium oxalate as well as the diazene. *tert*-Butyldiazene is too unstable to be observed under our conditions. Identical data were obtained in air and in oxygen-free solution. The shift of λ_{max} to shorter wavelengths in water is expected for an $n \rightarrow \pi^*$ transition.[16] The magnitude of the absorption coefficients supports a trans configuration for the diazenes.[2,17]

TABLE III

ABSORPTION DATA FOR ALKYLDIAZENES

R—N=NH R =	In H_2O λ_{max}, nm (ϵ_{max})[a]	Other solvents λ_{max}, nm (ϵ_{max})[b]
CH_3	350 (24)	361 (18) (C_2H_5OH) 362 (CH_3CN)
CH_3CH_2	356 (22)	367 (18) (C_2H_5OH)
$CH_3CH_2CH_2$	357 (24)	
$(CH_3)_2CH$	360 (22)	368 (20) (C_2H_5OH)

[a] This work. [b] Reference 17.

Reaction of Alkyldiazenes with Aqueous Acid.—Acidification of an alkyldiazene solution causes instantaneous decomposition of the diazene. The reaction of methyldiazene with acid was studied by adding room temperature 0.9 *M* sulfuric acid to $CH_3N{=}ND$ frozen at $-196°$. Decomposition is complete within the time of mixing. The products are methane, methane-d_1, nitrogen, methanol, methylhydrazine, 1,1-dimethylhydrazine, methyl sulfate, and hydrazine. Together these account for all of the original methyldiazene. Data are summarized in Table IV which shows that the relative distribution of products is similar in each run. Tests for formaldehyde, dimethyl ether, 1,1,1-trimethylhydrazine, 1,2-dimethylhydrazine, and the methylamines were negative.

A set of equations that can account for the products is

$$CH_3N{=}NH + H^+ \longrightarrow CH_3NH{=}NH^+ \qquad (4)$$

$$CH_3NH{=}NH^+ \longrightarrow CH_3^+ + HN{=}NH \qquad (5)$$

$$HN{=}NH + CH_3N{=}NH \longrightarrow CH_3NHNH_2 + N_2 \qquad (6)$$

$$2HN{=}NH \longrightarrow N_2H_4 + N_2 \qquad (7)$$

$$CH_3^+ + H_2O \longrightarrow CH_3OH + H^+ \qquad (8)$$

$$CH_3^+ + CH_3NHNH_2 \longrightarrow (CH_3)_2NNH_2 + H^+ \qquad (9)$$

$$CH_3^+ + HOSO_3^- \longrightarrow CH_3OSO_3^- + H^+ \qquad (10)$$

$$CH_3^+ + N_2H_4 \longrightarrow CH_3NHNH_2 + H^+ \qquad (11)$$

$$CH_3NH{=}NH^+ \longrightarrow CH_4 + N_2 + H^+ \qquad (12)$$

Because of the apparently rapid exchange of the N—H proton of $CH_3N{=}NH$ (*vide infra*) the reactions are written assuming $CH_3N{=}ND$ has exchanged entirely to $CH_3N{=}NH$, though this may not and need not be the case. The fact that CH_4 is the major methane product of $CH_3N{=}ND$ is compatible either with complete exchange or with donation of the fourth hydrogen by solvent.

The proposed reactions provide for loss of methyldiazene in steps 5, 6, and 12. The methylcarbonium

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(15) R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, **86**, 745 (1964).

(16) (a) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 187. (b) Gaseous $CH_3N{=}ND$ shows a broad band at λ_{max} = 362 nm.

(17) T. Tsuji and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 1992 (1971).

TABLE IV

PRODUCTS FROM THE ACID DECOMPOSITION OF $CH_3N{=}ND$ IN 0.9 M H_2SO_4[a]

Amt diazene added[b]	CH_4	CH_3D	N_2	CH_3OH	CH_3NHNH_2	N_2H_4	$CH_3OSO_3^-$	$(CH_3)_2NNH_2$	1/2(total N)	Total C
1.8 ± 0.2	0.18 ± 0.10	Trace	1.03 ± 0.10	0.66	0.83	0.10	0.15	0.10	2.06	2.02
2.1 ± 0.2	0.21 ± 0.10	Trace	1.14 ± 0.10	0.75	0.91	0.11	0.17	0.11	2.27	2.26

[a] All amounts in millimoles. Analytical uncertainties ±5%, unless otherwise indicated. [b] Calculated by measuring the volume of liquid $CH_3N{=}ND$ and assuming its density to be the same as that of azomethane.

ion generated in step 5 serves as a methylating agent in steps 8–11, while the diazene, HN=NH, produced in step 5 serves as a reducing agent in steps 6 and 7. Since step 5 followed by step 6 has the same consequence as step 5 occurring twice followed by steps 7 and 11, it is not possible to uniquely determine the contribution from steps 6, 7, and 11. Within experimental error, the product distribution (Table IV) can be accounted for by any combination of the two sequences. The two extreme viewpoints assume either no contribution from step 6 or no contribution from step 11. However, even if step 11 is unimportant, step 7 must still occur to an extent sufficient to produce the observed amount of hydrazine. Hydrogenation of diazene as in steps 6 and 7 is known to be rapid.[18] The greater role of step 5 *vs.* step 12 as shown by the low yield of methane suggests that diazene is a good leaving group.

Steps 8–11 are methylation reactions by the methylcarbonium ion. An alternate mechanism for these steps is nucleophilic attack at the carbon atom of $CH_3NH{=}NH^+$ by water, $HOSO_3^-$, N_2H_4, and CH_3NHNH_2 to form the methylated products and diazene. Our data cannot distinguish between these two possibilities. Close analogs to protonated diazenes are alkyldiazonium ions which are believed to undergo both types of reaction.[19a] Since the concentration of water in our system is much larger than that of either $HOSO_3^-$, N_2H_4, or CH_3NHNH_2, it is not surprising that methanol is a major methylation product. The formation of 1,1- rather than 1,2-dimethylhydrazine is consistent with the known tendency for further methylation to take place on the already substituted nitrogen.[19b] As expected methyl chloride was formed when hydrochloric acid was substituted for sulfuric acid.

Alkylcarbonium ions containing more than one carbon atom can also undergo elimination to form olefins. Although *n*-propyldiazene is not isolable in pure form, we did acidify the alkaline solution in which *n*-propyldiazene is produced and found propylene among the gaseous products.

Two known routes to methane and nitrogen from methyldiazene have been omitted from our mechanism. First, the gas-phase decomposition is considered to be insignificant because the pressure over the reaction solution stabilized immediately after mixing, whereas the pressure should rise slowly over about 1 hr if methyldiazene were decomposing in the gas phase. This observation, along with the detection of only trace amounts of CH_3D, also shows that vaporization of $CH_3N{=}ND$ during mixing is not important. Second, the bimolecular decomposition of methyldiazene is omitted largely because this reaction would appear to be too slow. Assuming the rate constant of 0.03 M^{-1} sec^{-1} at 25° found in ethanol[17] holds in our aqueous system, about 22 sec would be required for 10% of a 0.2 M $CH_3N{=}NH$ solution to decompose by the bimolecular route. Our reaction is essentially instantaneous at a temperature near 0°.

The rearrangement of $CH_3N{=}NH$ to the hydrazone (eq 13), a reaction known for azomethane in acid,[20]

$$CH_3N{=}NH \xrightarrow{H^+} CH_2{=}NNH_2 \xrightarrow{H_2O} CH_2O + N_2H_4 \qquad (13)$$

also must be insignificant since tests for formaldehyde were negative.

Exchange of the N—H Proton of Methyldiazene.—Like amine, hydrazine, and imine protons, the N—H proton of methyldiazene also undergoes facile exchange in aqueous solution. When $CH_3N{=}NH$ is added to a buffered D_2O solution (pH 4–13) and the diazene reisolated a few minutes later, the gas-phase infrared spectrum shows the bands characteristic of $CH_3N{=}ND$. On this time scale $CH_3N{=}NH$ would not yet have completely decomposed. We take the absence of even the sharp, intense 844-cm^{-1} band of $CH_3N{=}NH$ to signify complete exchange of the N—H proton. Therefore in our experiments on the decomposition of methyldiazene in acidic and alkaline solutions, it was probably the solvent and not the isomer of methyldiazene used to make the solution that determined whether the N—H or N—D isomer was being studied.

Reaction with Oxygen.—A known feature of monosubstituted diazene chemistry in solution is a sensitivity to reaction with oxygen.[1] In the gas phase this reaction becomes particularly rapid and violent. Thus gaseous $CH_3N{=}NH$ reacts explosively with oxygen at room temperature; $CH_3N{=}ND$ also reacts rapidly, but not violently, with oxygen. This difference in reactivity is probably a consequence of the primary isotope effect. The greater violence of the $CH_3N{=}NH$–O_2 reaction causes fragmentation of the CH_3 group which leads to a richer set of products. For $CH_3N{=}NH$ the major carbon-containing products are CO_2, CO, and CH_4 with smaller amounts of $CH_2{=}CH_2$, $HC{\equiv}CH$, and CH_3OH also being formed. $CH_3N{=}ND$ gives only CH_3D and CH_3OD. Molecular nitrogen is the only nitrogen-containing product in each case. The cuprous chloride complex of methyldiazene, $(CH_3N{=}NH)CuCl$, inflames spontaneously in air to give similar products.[8] These reactions undoubtedly proceed by a free-radical chain mechanism, but it would be mere speculation to propose a set of elementary steps at this time.

Physical Properties of Methyldiazene.—Methyldiazene and, to a lesser extent, ethyldiazene are sufficiently volatile to be coaxed out of an aqueous solution and isolated as pure substances. The melting and boiling points were measured for $CH_3N{=}ND$ because of its greater kinetic stability than $CH_3N{=}NH$.

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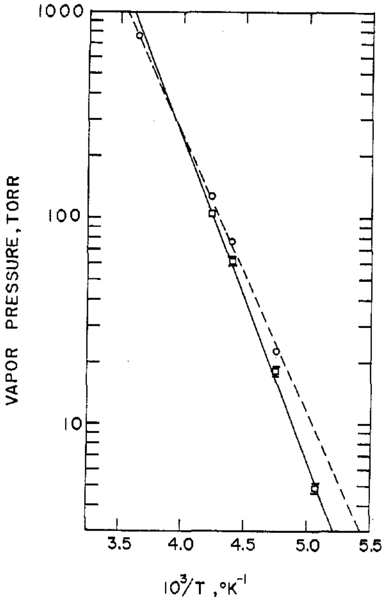

Figure 1.—Plot of log (vapor pressure) *vs.* reciprocal temperature: circles, azomethane; squares, methyldiazene-*N-d* in contact with *trans*-chlorohydridobis(triethylphosphine)platinum-(II).

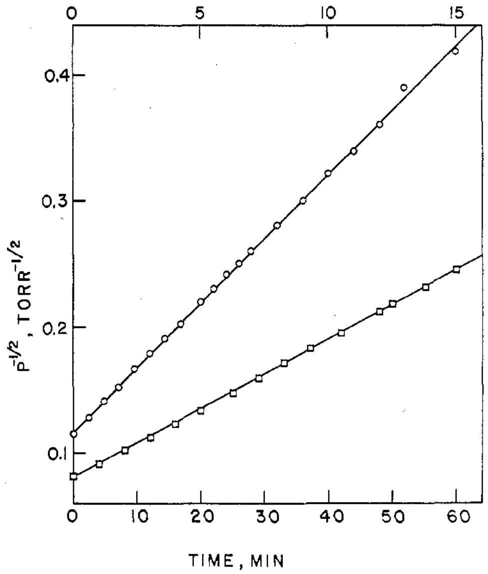

Figure 2.—Three-halves-order kinetic plot of the gas-phase decomposition of methyldiazenes: circles, $CH_3N{=}NH$; squares, $CH_3N{=}ND$. Rate constants are 0.93 and 0.11 $M^{-1/2}$ sec^{-1}, respectively, at 23 ± 1°. Upper time scale applies to circles; lower time scale to squares.

The pale yellow solid $CH_3N{=}ND$ melts sharply at $-122 \pm 1°$ to a bright yellow liquid. The boiling point of this liquid could not be measured directly, but was estimated by extrapolation of vapor pressure data from lower temperatures. Even at $-76°$ the decomposition of $CH_3N{=}ND$ in the liquid phase is sufficiently rapid to make accurate vapor pressure estimates impossible. Not even a temporary constancy of the pressure could be noted because of the constant evolution of methane and nitrogen. However, in other work involving methyldiazene we found that this liquid-phase decomposition was effectively slowed when some *trans*-chlorohydridobis(triethylphosphine)platinum(II) was in contact with the liquid.[21] Presumably some of the platinum complex dissolves in the liquid methyldiazene and scavenges an intermediate in the decomposition reaction. We believe that the vapor pressure readings obtained in the presence of the platinum complex are true values because (1) the same vapor pressure is obtained at both 20:1 and >200:1 molar excess of diazene, and (2) the diazene could be distilled off the platinum complex unchanged after measurements were completed. The data for $CH_3N{=}ND$ and, for comparison, azomethane are plotted in Figure 1. The calculated boiling point for $CH_3N{=}ND$ is $-2 \pm 5°$; azomethane boils at 1.5°. The enthalpies and entropies of vaporization also can be calculated from Figure 1 since for each line slope $= -\Delta H_v°/2.3R$ and $\Delta S_v° = \Delta H_v°/T$. For $CH_3N{=}ND$, $\Delta H_v° = 7140 \pm 350$ cal/mol and $\Delta S_v° = 26.3 \pm 1.8$ eu; for azomethane, $\Delta H_v° = 6150 \pm 150$ cal/mol and $\Delta S_v° = 22.4 \pm 0.5$ eu.

On the basis of their relative molecular weights methyldiazene is expected to boil about 50° lower than azomethane,[22] whereas within experimental error the boiling points are essentially identical. This suggests that hydrogen bonding is important in liquid methyldiazene. Hydrogen bonding can occur between the N—H hydrogen atom of one molecule and the lone pair of electrons on a nitrogen atom of another molecule. Hydrogen bonding is not important in azomethane since this molecule has only C—H hydrogen atoms. The larger values of $\Delta H_v°$ and $\Delta S_v°$ for $CH_3N{=}ND$ compared with azomethane also support this interpretation of stronger intermolecular forces in $CH_3N{=}ND$.

Gas-Phase Decomposition of Methyldiazene.—In the gas phase methyldiazene and *N*-deuteriomethyldiazene decompose according to the stoichiometric eq 14 and 15, respectively. At comparable pressures of

$$CH_3N{=}NH(g) \longrightarrow CH_4(g) + N_2(g) \qquad (14)$$

$$CH_3N{=}ND(g) \longrightarrow CH_3D(g) + N_2(g) \qquad (15)$$

the diazenes the N–D isomer decomposes substantially more slowly than the N–H isomer. The rate of decomposition is reflected in the increase in pressure of the gaseous sample as one molecule of diazene forms two molecules of products. The pressure of undecomposed diazene at time t, P_D, is given by $P_D = P_\infty - P_t$ where P_∞ is the total pressure of the sample after complete decomposition and P_t is the total pressure at time t. Because of the relatively rapid rate of decomposition some products have already formed when the first pressure reading is taken following vaporization of the frozen diazene. This problem was more severe for the N–H isomer where only the last 80–100 Torr of diazene decomposition could be followed from a total initial diazene sample of 150–200 Torr (determined from P_∞ and the stoichiometry). For the N–D isomer the last 110–150 Torr of diazene decomposition was followed for samples initially 120–170 Torr in diazene. In all cases for these high-pressure studies a plot of $(1/P_D)^{1/2}$ *vs.* times (Figure 2) gave a linear relationship for at least 90% of the decomposition. Neither first- nor second-order plots fit the data. The rate law implied is

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[21] D. F. Starks and M. N. Ackermann, unpublished work.

[22] Compare propene and *trans*-2-butene which boil at -47.8 and 0.9°, respectively.

$$dP_D/dt = -k_{obsd}P_D^{3/2}$$

The values of k_{obsd} based upon three kinetic runs at 23 ± 1° are 0.93 ± 0.08 and 0.11 ± 0.01 $M^{-1/2}$ sec^{-1} for $CH_3N{=}NH$ and $CH_3N{=}ND$, respectively.

A reasonable mechanism to account for these data is

$$CH_3N{=}NH \xrightarrow{k_1} CH_3\cdot + \cdot N{=}NH \quad \text{initiation} \tag{16}$$

$$\cdot N{=}NH \xrightarrow{k_2} N_2 + H\cdot \tag{17}$$

$$H\cdot + CH_3N{=}NH \xrightarrow{k_3} H_2 + CH_3N{=}N\cdot \tag{18}$$

$$\left.\begin{aligned} CH_3\cdot + CH_3N{=}NH &\xrightarrow{k_4} CH_4 + CH_3N{=}N\cdot \quad (19) \\ CH_3N{=}N\cdot &\xrightarrow{k_5} CH_3\cdot + N_2 \quad (20) \end{aligned}\right\} \text{propagation}$$

$$2CH_3\cdot \xrightarrow{k_6} C_2H_6 \quad \text{termination} \tag{21}$$

A long chain is suggested since neither hydrogen gas nor ethane was found in gas chromatographic and mass spectrometric analyses of the products. Also absent in the products are hydrazines and tetrazines, and, in $CH_3N{=}ND$ decomposition, the level of CH_4 did not exceed that expected from some $CH_3N{=}NH$ impurity. These observations suggest that the side reactions of addition of radicals to the N=N double bond and abstraction of a C—H hydrogen from methyldiazene are unimportant. Apparently these reactions are too slow to compete with abstraction of the N—H hydrogen in eq 19.

As a further test of the proposed mechanism we examined a gaseous mixture of $CH_3N{=}ND$ and $CD_3N{=}NH$. This mixture should produce both CD_3 and CH_3 radicals which may then abstract either the N—H hydrogen from $CD_3N{=}NH$ or the N—D deuterium from $CH_3N{=}ND$. As expected substantial amounts of the cross products CD_4 and CH_4 were formed in addition to CH_3D and CD_3H.

Making the usual steady-state assumptions for the proposed mechanism the observed rate constant derived is $k_{obsd} = k_4(k_1/k_6)^{1/2}$. The isotope effect in k_{obsd} arises through k_4 which reflects the abstraction of a hydrogen or deuterium atom by the methyl radical. The observed k_H/k_D ratio of 8.5 ± 1.6 is in good agreement with that calculated by the simple assumption that the primary hydrogen isotope effect can be accounted for entirely by zero-point-energy differences. If only the N—H stretching frequency is considered to be important k_H/k_D is calculated to be 7.2.[23a] If the N—H bend is included as well a value of 8.7 is obtained.[23b]

In the absence of further information such as relative bond energy data for the N—H and N—C bonds in methyldiazene, one might propose that the first step in the mechanism (eq 16) could alternatively be

$$CH_3N{=}NH \xrightarrow{k_1} CH_3N{=}N\cdot + \cdot H$$

with the second step (eq 17) no longer needed. The rate law and the expression for k_{obsd} remain unchanged, but now k_1 as well as k_4 includes an isotope effect. From the arguments in the previous paragraph the predicted k_H/k_D values become 19.3 and 25.6 (the previous values raised to the $^3/_2$ power). Since these values are so much larger than the experimental ratio of 8.5 ± 1.6, we favor C—N rather than N—H bond breaking in the initiation step.

The above features of methyldiazene decomposition may be compared with observations on the symmetrically dialkylated diazene, azomethane (1,2-dimethyldiazene). To begin with azomethane, having only N–C bonds, is stable at room temperature. Decomposition may be induced thermally[24a,b] or photolytically[24c] and is believed to involve both a unimolecular and a short chain (2–3 in length) radical mechanism. Both radical addition to the N=N double bond[24c] and C—H abstraction[24b,c] are important processes in azomethane decomposition. Thus, the presence of the N—H bond has important consequences for the reactivity of methyldiazene.

Vibrational Spectra of Methyl- and Ethyldiazenes.—In an earlier communication we concluded that methyldiazene had the trans configuration.[2] One argument concerned the similarity of λ_{max} and ϵ of the n → π* transition of methyldiazene to that of *trans*- and not to that of *cis*-azomethane; the other argument involved a comparison of the spacing of the rotational structure of the N—H and N—D out-of-plane bending vibration appearing in the gas-phase infrared spectra of $CH_3N{=}NH$ and $CH_3N{=}ND$, respectively. The structural parameters assumed for methyldiazene and the assignment of a trans configuration have subsequently been verified by a microwave study of $CH_3N{=}ND$.[25]

We are presently in the process of attempting a complete vibrational assignment of methyldiazene which will be reported in detail in a subsequent paper. However, it seems appropriate to describe here several distinctive features that appear to be generally characteristic of monosubstituted diazenes and thus are useful in the identification of such molecules. These conclusions are drawn from examining the spectra of four methyldiazenes, $CH_3N{=}NH$, $CH_3N{=}ND$, $CD_3N{=}NH$, and $CD_3N{=}ND$, and two ethyldiazenes, $CH_3CH_2N{=}NH$ and $CH_3CH_2N{=}ND$.

The type A N—H or N—D stretching band at 3120–3130 or 2280–2320 cm^{-1}, respectively, is the most useful feature for identifying a monosubstituted alkyldiazene. The frequency of this band is only slightly altered by changes in the alkyl group at the other end of the molecule. In the parent diazenes, HN=NH and DN=ND, the corresponding band is the N—H or N—D asymmetric stretch. This band has been identified at 3120 cm^{-1} in gaseous N_2H_2[26] and at 3095 and 2291 cm^{-1} in the solid phase spectra of N_2H_2 and N_2D_2, respectively.[27] The N—H and N—D out-of-plane bends show ranges of 725–845 and 625–680 cm^{-1}, respectively, and are not particularly useful as group frequencies. In the parent diazenes the corresponding bands have been assigned at 1359 cm^{-1} (N_2H_2) and 999 cm^{-1} (N_2D_2).[27] If correct these are surprisingly high values when compared with the monosubstituted diazenes and with the corresponding C—H bend in ethylenes. The N=N stretch at 1540–1575 cm^{-1} is a good though weak group frequency

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[23] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, Chapter 2: (a) p 20, eq 2-10; (b) p 22, eq 2-12.

[24] (a) C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 975 (1959); (b) W. Frost and O. K. Rice, *Can. J. Chem.*, **41**, 562 (1963); (c) D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **65**, 175 (1969).

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and is in agreement with the assignments in azomethane (1575 cm^{-1}),[28] *trans*-difluorodiazene (1522 cm^{-1}),[29] N_2H_2 (1552 cm^{-1}),[27] and N_2D_2 (1498 cm^{-1}).[27] We consistently found the N=N stretching band to be more intense in the N—D isomer of each pair of diazenes. Finally, each monosubstituted diazene has as its lowest frequency infrared band in the 400–4000-cm^{-1} region a type A band at 480–550 cm^{-1} which we assign to the C—N=N bend. Supporting this assignment are the C—N=N bend of azomethane at 596 cm^{-1} [28] and the C—C=C bend of propene at 417 cm^{-1}.[30]

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The Borane-Catalyzed Condensation of Trisilazane and *N*-Methyldisilazane[1]

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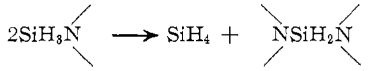
Diborane, B_5H_9, 1-BrB_5H_8, and 2-BrB_5H_8 catalyze the condensation of $(SiH_3)_3N$ and $CH_3N(SiH_3)_2$ in the liquid phase to yield silane and silazane oligomers and/or polymers. Under carefully controlled reaction conditions, the initial condensation oligomers, $[(SiH_3)_2N]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$, can be obtained in good yields. Chemical and spectral characterization data for the new silazanes are given. A possible mechanism for the condensation is discussed.

Introduction

Silazane condensation reactions of the type



$$2SiH_3N\!\!< \;\longrightarrow\; SiH_4 + \;>\!\!NSiH_2N\!\!< \qquad (1)$$

are of interest for the synthesis of silicon–nitrogen bonds. Base-promoted reactions of this general type are well established.[2–5] Since silazanes are amphoteric, Lewis acid catalyzed reactions might also be expected if the acids are ones which do not readily cleave silicon–nitrogen bonds. Diborane might be expected to qualify as such an acid since it does not complex strongly enough with $(SiH_3)_3N$ or $CH_3N(SiH_3)_2$ to form an adduct or readily cleave the Si–N bonds. This is in contrast to the behavior of the stronger acid B_2H_5Br.[6] These considerations along with our interest in finding new routes to group IV–group V ternary hydrides has led us to examine reactions of $(SiH_3)_3N$ and $CH_3N(SiH_3)_2$ in the presence of B_2H_6, B_5H_9, 1-BrB_5H_8, and 2-BrB_5H_8. With these relatively weak acids, condensation does occur and we have succeeded in isolating and characterizing the initial condensation oligomers, $[(SiH_3)_2N]_2SiH_2$ and $(SiH_3NCH_3)_2SiH_2$.

Experimental Section

Apparatus.—All work was carried out in a standard high-vacuum system.[7,8] Vapor pressure *vs.* temperature data were collected with an all-glass immersible tensimeter (mercury manometer). Melting points were obtained by the Stock magnetic plunger technique. Mass spectra were obtained on Varian MAT CH-5 and CH-7 spectrometers (ionizing voltage 70 eV). Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer on gaseous samples in a 10-cm cell equipped with KBr windows. Proton nmr spectra were obtained at 60.0 and 100.0 MHz on Varian A-60A and HA-100 spectrometers, respectively. Proton chemical shifts are reported relative to internal $(CH_3)_4Si$. Boron-11 nmr data were obtained with a Varian HA-100 equipped with standard 32.1-MHz probe and rf unit accessories.

Materials.—Diborane,[9] 1-BrB_5H_8,[10] 2-BrB_5H_8,[11] and $(SiH_3)_3N$[12] were prepared and purified using standard methods. The $CH_3N(SiH_3)_2$[13] was prepared using a reaction analogous to that described for $(SiH_3)_3N$. Pentaborane(9) (Callery Chemical Co.), HBr, and HCl (Matheson) were purified by routine fractional condensation techniques. In every case, compound purity was established by comparison of infrared, nmr, and physical property data with previously published values.

Borane-Catalyzed Condensations.—Typical borane-catalyzed condensation reactions of $(SiH_3)_3N$ and $CH_3N(SiH_3)_2$ are shown in Table I. In each case the reactants were condensed into 5–10-ml reaction tubes and allowed to warm to the indicated reaction temperature. In all experiments shown in Table I a liquid phase was present during the reaction. After the specified time, reaction materials were removed to the vacuum line, separated by routine fractional condensation, and characterized as outlined below. No hydrogen was formed in any of the reactions. Known components were characterized by comparison of their physical and/or spectral properties with literature values (confirmation methods in parentheses): SiH_4 (ir spectrum[14]), B_2H_6 (ir spectrum[15] and −112° vapor tension[16]), B_5H_9 (ir[17] and ^{11}B nmr[18] spectra), 1-BrB_5H_8 (^{11}B nmr spectrum[18]), 2-BrB_5H_8 (^{11}B

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[1] (a) Supported by National Science Foundation Grant GP-23575. (b) Based in part on M.S. Thesis of William M. Scantlin, Sept 1971, University of Colorado.

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