trum indicating pure material. Norcamphane was prepared by hydrogenating a sample of bicyclo[2.2.1]heptadiene kindly supplied by the Shell Chemical Co.

Chlorinations were carried out in small sealed tubes using a 5–10-fold excess of hydrocarbon. This excess is important in isomer distribution studies to eliminate complications due to polychlorination. Measured amounts of hydrocarbon and solvent were placed in the tubes, which were then attached to a vacuum line and measured quantities of chlorine condensed in from a calibrated receiver. The tubes were finally degassed with liquid nitrogen cooling and sealed. Reactions were accomplished by placing the tubes in a thermostat and irradiating with a 100-watt incandescent light at approximately 25 cm. until the chlorine color had disappeared. When benzene was used as solvent, some hexachlorocyclohexane sometimes was formed. While this required separation before analysis, its formation does not interfere with our relative reactivity measurements. The molar concentration of solvents employed was determined by the ratio of solvent to substrate being chlorinated the balance of the system being substrate; see Table VI below for actual examples.

Analyses were carried out by gas chromatography, using either a Perkin–Elmer Vapor Fractometer or a Wilkens Instrument and Research Inc. Aerograph and whichever of several column substrates gave the most satisfactory resolution. Each reaction mixture was analyzed in duplicate or triplicate, and ratios of peak heights or areas usually agreed to within 2–3%. Experimental errors given in Tables I–V represent the spread of independent experiments.

In competitive halogenation of different molecules relative reactivities were determined by change in peak height or area relative to an internal standard (usually the solvent), and Table VI presents representative experimental results on pairs of cycloparaffins, chlorinated at 68° in CCl_4. Cyclohexane and cyclopropane differ too much in reactivity for accurate direct comparison. Accordingly cyclopropane was chlorinated with neopentane, relative reactivity *vs.* cyclohexane (determined independently) 0.555. Relative reactivities were calculated from original data *via* equation 1, assuming only that ratios of peak heights relative to internal standards before and after reaction were proportional to the amounts of substrate present. Thus in the first experiment of Table VII

$$\frac{\text{react. of cyclopentane}}{\text{react. of cyclohexane}} = \frac{\log(1.385/1.151)}{\log(1.909/0.712)} = 0.76$$

In experiments involving chlorine atom attack at different points on the same molecule to yield isomeric products, relative reactivities were determined by the relative amounts of chlorides produced (using a large hydrocarbon/chlorine ratio to suppress further chlorination). The chlorination of *n*-butyl chloride represents the most complicated case, but clean separation was obtained using the "A" column in the Perkin–Elmer instrument at 115° and 25 p.s.i. helium pressure. Retention times observed were 1,1-dichlorobutane, 5.4 min.; 1,2-, 6.9 min.; 1,3-, 8.8 min.; 1,4-, 16.2 min. Experiments on known mixtures showed that peak areas were proportional to concentrations of each component. The "A" column was used also for the separation of isomers in the chlorination of ethyl chloride (at 50°), 2,3-dimethylbutane (at 114°) and for the analysis of the hydrocarbon mixtures in Table I (at 114°). Resolution of 1- and 2-chlorobutane in the presence of benzene (Table II) required "A" and "C" columns in series at 80°.

TABLE VII

REPRESENTATIVE RESULTS IN CHLORINATION OF CYCLOPARAFFINS AT 68° IN CCl_4[d]

Compound	Ml.	Retention time	R_0[b]	R[c]
C_5H_{10}	1.1	2.5[a]	1.385 ± 0.035	1.151 ± 0.031
C_6H_{12}	1.1	5.3[a]	.909 ± .051	.712 ± .027
CCl_4	2.0	6.5[a]		
C_4H_8	0.2	1.4	.0965 ± .007	0.368 ± .002
C_5H_{10}	1.9	3.2	.715 ± .038	.208 ± .003
CCl_4	2.0	8.8		
C_3H_6	1.1	0.9	.477 ± .009	.303 ± .012
Neo-C_5H_{12}	1.1	1.01	.752 ± .012	.0915 ± .003
CCl_4	2.0	8.8		
n-C_4H_{10}	1.1	0.9	1.42 ± .013	.886 ± .003
C_5H_{10}	1.1	3.2	.734 ± .013	.421 ± .004
CCl_4	2.0	8.8		

[a] At 68°. [b] Ratio of peak height to CCl_4 before reaction. [c] Ratio of peak height to CCl_4 after reaction. Experimental errors here and in R_0 are the spread of 3 analyses on the same reaction mixture. [d] Using 0.3 cc. of Cl_2, analysis with Perkin–Elmer Fractometer, 2 meter "A" column, 25 p.s.i. helium Pressure at 50° unless noted.

The major product from the chlorination of norcamphane was separated and purified on an "A" column at 142°, $n^{25}D$ 1.4837, lit. 1.4824[15] (other reported values range up to 1.4849). It rapidly liberated chloride ion on treatment with alcoholic $AgNO_3$.

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Syntheses by Free-radical Reactions. VIII. Reactions of Amino Radicals with Olefins

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A new synthesis of diamines has been found in the additive dimerization of dienes with amino radicals generated from hydroxylamine by reducing ions. Thus, 1,8-diamino-2,6-octadiene was obtained from butadiene, hydroxylamine and a titanium(III) salt. In a similar reaction, 2-butene has given 3,4-dimethyl-2,5-hexanediamine. Use of ethylene has given products containing from one to several ethylene units per molecule. With titanium(III) as reducing agent these products are monoamines and diamines, whereas with vanadium(III) the chief products are aminoalcohols.

Amino radicals have been shown to be intermediates in the reaction of hydroxylamine with a titanous salt,[1] and radicals produced in this way

$$NH_3OH^+ + Ti^{3+} \longrightarrow NH_2\cdot + H_2O + Ti^{4+}$$

have been used to initiate vinyl polymerization.[2] The reaction of amino radicals with benzene has been reported to yield an unstable intermediate which decomposed to ammonia, aniline and biphenyl.[3] Toluene gave similar results, and cyclohexene formed cyclohexylamine.

It has now been found that amino radicals generated from hydroxylamine undergo additive dimer-

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[1] P. Davis, M. G. Evans and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951).

[2] E. Howard, U. S. Patents 2,683,140, July 6, 1954, and 2,567,109, Sept. 4, 1951.

[3] H. Seaman, P. J. Taylor and W. A. Waters, *ibid.*, 4690 (1954).

ization[4] with olefins to yield diamines containing two units of the unsaturated compound. The additive dimerization can be represented as

$$NH_2\cdot^{(5)} + M \longrightarrow NH_2{-}M\cdot$$
$$2NH_2{-}M\cdot \longrightarrow NH_2{-}M{-}M{-}NH_2$$

in which M represents a unit of composition corresponding to that of the diene or monoölefin employed. It is conveniently carried out at 0 to 30° by introducing a hydroxylamine salt and a solution of a titanium(III) or vanadium (III) salt in stoichiometric amount into a well-stirred solution of the unsaturated compound in acidic aqueous methanol.

The mixture of additive dimers obtained from butadiene and amino radicals was principally 1,8-diamino-2,6-octadiene, as shown by the formation of octamethylenediamine in at least 70% yield upon hydrogenation. The octamethylenediamine formed was identified by its physical properties and by a comparison of its dibenzamide derivative with an authentic sample. Small quantities of branched-chain unsaturated 8-carbon diamines presumed to have been formed by the incorporation of butadiene by 1,2-addition rather than by 1,4-addition and also higher-boiling amines were formed in low yield. Similar syntheses using isoprene, cyclopentadiene, cyclohexadiene and methylpentadiene also gave diamines as additive dimers but in lower yields. In a limited study, methylamino radicals were found to undergo additive dimerization with butadiene.

Terminally unsaturated olefins such as ethylene, propylene and isobutylene reacted with amino radicals generated from titanium(III) salts and hydroxylamine to form complex mixtures of mono- and diamines. Thus, ethylamine, butylamine, hexylamine, octylamine and octamethylenediamine have been identified among the products obtained from ethylene in various experiments. Butylamine was the product always formed in highest yield. The formation of monoamines involves the reduction of an intermediate free radical, probably by a Ti^{3+} ion

$$NH_2CH_2CH_2\cdot + Ti^{3+} \longrightarrow NH_2CH_2CH_2^- + Ti^{4+}$$
$$NH_2CH_2CH_2^- + H^+ \longrightarrow NH_2CH_2CH_3$$

Amino radicals added preferentially to the terminal methylene group of an olefin as shown by the formation of propylamine and isobutylamine from propylene and isobutylene, respectively. The main product from propylene was not propylamine but was a mixture of 6-carbon monoamines, with 2-methylpentylamine as probably the main component. The many other amines obtained from these olefins have not been completely characterized.

In contrast to the reactions of terminal olefins, 2-butene reacted with amino radicals to give as the principal product 3,4-dimethyl-2,5-hexanediamine and 1-methylpropylamine in yields of 18 and 15%, respectively, based on the hydroxylamine consumed. The reduction of hydroxylamine to ammonia was the principal competitive reaction. Interestingly, 1-hexene also reacted with amino radicals forming a 12-carbon diamine, presumably 2,3-dibutyl-1,4-butanediamine, as the main product.

When ethylene was treated with hydroxylamine and vanadium(III) salts, the principal products were alkanolamines. For example, in one experiment carried out at room temperature in water, the following amines were obtained in the indicated yields based on vanadium sulfate: ethylamine (5%), butylamine (15%), ethanolamine (38%), 4-hydroxybutylamine (18%), and a small amount (4%) of unidentified higher-boiling amines. It seems likely the hydroxy group is formed by oxidation of the aminoalkyl radical with vanadium(IV) sulfate. Since titanium(IV) salts are weaker oxidizing agents than vanadium(IV) salts, they less readily effect oxidation of aminoalkyl radicals.

$$NH_3OH^+ + V^{3+} \longrightarrow \cdot NH_2 + V^{4+} + H_2O$$
$$\cdot NH_2 + nCH_2{=}CH_2 \longrightarrow \cdot(CH_2CH_2)_nNH_2$$
$$\cdot(CH_2CH_2)_nNH_2 + V^{4+} + H_2O \longrightarrow HO(CH_2CH_2)_nNH_2 + H^+ + V^{3+}$$

The reaction of benzene and toluene with amino radicals gave unstable amines that appeared to be identical with those reported recently.[3] However, by using a reaction mixture of acetic acid or formic acid and water instead of water alone the yields of these products were markedly improved over those previously reported. The initial amines from benzene and toluene decomposed when heated, yielding ammonia, biphenyl and presumably bitolyl, respectively. Aniline and *p*-toluidine were also obtained in small amounts.

The ultraviolet spectrum of the unstable amine from benzene indicated the absence of conjugated double bonds. Hydrogenation at low pressure using Adams catalyst yielded bicyclohexylamine and a diamine whose neutral equivalent and elemental analyses corresponded to a diaminobicyclohexyl.

The observed stoichiometry of the Ti^{3+}–NH_2OH reaction has indicated that reactions of amino radicals with solvents and halide ions may occur.

If excess titanium(III) is treated with hydroxylamine in the absence of other reactants, reduction to ammonia occurs as

$$NH_3OH^+ + Ti^{3+} \longrightarrow NH_2\cdot + H_2O + Ti^{4+} \qquad (1)$$
$$H^+ + NH_2\cdot + Ti^{3+} \longrightarrow NH_3 + Ti^{4+} \qquad (2)$$
$$(\text{or } NH_3^+\cdot + Ti^{3+} \longrightarrow NH_3 + Ti^{4+})$$

This sequence requires two moles of Ti^{3+} for each mole of hydroxylamine.

In the presence of butadiene, the amino radical may add to the diene before reduction occurs so that step 2 is replaced by step 3. By this reaction

$$NH_2\cdot + C_4H_6 \longrightarrow NH_2C_4H_6\cdot \longrightarrow \text{dimer} \qquad (3)$$

path, one mole of Ti^{3+} is consumed for each mole of hydroxylamine. The observed stoichiometry in the presence of butadiene has been approximately 1.05 moles of Ti^{3+} consumed per mole of hydroxylamine. This corresponds to 95% efficiency of step 3 in superseding step 2.

A number of solvents, *e.g.*, methanol, acetone, dimethylformamide, ethyl alcohol and isopropyl

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(4) D. D. Coffman and E. L. Jenner, THIS JOURNAL, **81**, 2872 (1958).

(5) It is believed that the actual species in the highly acidic media employed in this work are $NH_3\cdot^+$ radicals. For simplicity they are referred to as $NH_2\cdot$ in this paper.

alcohol, react with amino radicals by hydrogen extraction (equation 4) to yield radicals which are oxidized (step 5a or 5b) and thus furnish a chain reaction. When these processes occur, the Ti^{3+}/NH_2OH ratio falls below two (this is in systems containing no olefin), since in step 5a titanium(III) is regenerated and in 5b amino radicals are formed directly without the consumption of titanium(III).

$$NH_2\cdot + RH \longrightarrow R\cdot + NH_3 \qquad (4)$$

$$R\cdot + Ti^{4+} \longrightarrow R^+ + Ti^{3+} \qquad (5a)$$

$$\text{(followed by: } R^+ + H_2O \longrightarrow ROH + H^+\text{)}$$

$$R\cdot + NH_2OH \longrightarrow ROH + NH_2\cdot \qquad (5b)$$

Methanol is an especially reactive solvent. As shown in Table II, the Ti^{3+}/NH_2OH ratio was only 0.9 in an aqueous methanol solution as compared to 2.0 in water alone. It was found that the methanol was oxidized to formaldehyde in about 27% yield as determined by sulfite titration. *t*-Butyl alcohol was less reactive than methanol, and acetic acid was inert to amino radicals. The fact that methanol can be used as solvent for reactions of amino radicals with olefins indicates that the rate of the abstraction reaction 4 is much slower than the rate of addition of amino radicals to double bonds (3).

If a halide ion is added to the reaction system containing a diene, three new reactions become possible

$$H^+ + NH_2\cdot + X^- \longrightarrow NH_3 + X\cdot \qquad (6)$$

$$X\cdot + Ti^{3+} \longrightarrow Ti^{4+} + X^- \qquad (7)$$

$$X\cdot + C_4H_6 \longrightarrow XC_4H_6\cdot \longrightarrow \text{dimer} \qquad (8)$$

If steps 6 and 7 occur, this is revealed by an increase in the Ti^{3+}/NH_2OH ratio. If 6 and 8 take place, there is no change in the stoichiometry, but the product is a halide rather than an amine.

When the synthesis of diaminoöctadiene was attempted in the presence of chloride ion, no interference by the latter was observed. The Ti^{3+}/NH_2OH ratio held at 1.05, and the product was the diamine. Bromide ion, however, was extremely reactive with amino radicals, and reaction 6 superseded formation of diamine (reaction 3). Both reactions 7 and 8 occurred. The stoichiometry changed to a Ti^{3+}/NH_2OH ratio of 1.65 (rather than 1.05), demonstrating the occurrence of step 7. This ratio indicates that the sequence of steps 6 and 7 accounts for 60–65% of the amino radicals. Also, step 8 was indicated by the fact that the additive dimer formed was the bromide rather than the diamine. Thus, there are two independent pieces of evidence pointing to the occurrence of step 6.

Experimental

I. **Materials.**—The aqueous titanium trichloride employed was purchased from the Fisher Scientific Co. as 15–20% solutions containing a considerable quantity of zinc salts. Vanadium(III) sulfate solutions were prepared by catalytic (Adams catalyst) hydrogenation of vanadyl sulfate solutions at 25–50° and atmospheric pressure. The precise concentration of both solutions was determined by titration with a standard ferric alum or ferric chloride solution using ammonium thiocyanate as indicator. The other chemicals used were commercial products.

II. **Reaction of Amino Radicals with Butadiene.**[6]—To a well-stirred mixture of 104.3 g. (1.5 moles) of hydroxylamine hydrochloride, 81 g. (1.5 moles) of butadiene, 150 g. of sulfuric acid, 600 ml. of methanol and 300 ml. of water were added over a period of 10 minutes at −7°, 81 g. (1.5 moles) of butadiene and 500 ml. (0.75 mole) of titanium(III) chloride solution. The reaction mixture was allowed to warm to room temperature after the additions had been completed, and alkali was added in sufficient quantity to precipitate titanium hydroxide. The titanium hydroxide was removed by filtration, and the filtrate was concentrated. Salts that precipitated were removed by filtration, and the filtrate was made strongly alkaline with potassium hydroxide. The amine layer was separated and distilled. There was obtained 57 g. (42% yield based on titanous(III) chloride) of isomeric diaminoöctadiene fractions distilling in the range 70–110° (4.7 mm.).

Anal. Calcd. for $C_8H_{12}N_2$: neut. equiv., 70.1. Found: neut. equiv., 70.6.

The residue was a dark brown rubbery resin which contained 10.8% nitrogen.

The above diamine (46 g.) was hydrogenated using dioxane as a solvent with a palladium-on-carbon catalyst. The solution was concentrated, and the product was distilled through a spinning band column at a 25:1 reflux ratio to obtain eight fractions distilling from 86 to 93° at 3.7 mm. All of the fractions had neutral equivalents between 71.2 and 72.8 (calculated for a saturated 8-carbon diamine, 72.1). Fractions 2, 3 and 4 were partly solid at room temperature, and fractions 5 to 8 solidified completely at room temperature. The total amount of the solid fractions was 31.9 g., m.p. 46–50°. A dibenzamide derivative prepared from the solid fractions melted at 174–175°. A mixture of this dibenzamide with the dibenzamide prepared from an authentic sample of octamethylenediamine melted at 174–175°. The liquid fractions amounted to 8.3 g. and contained some octamethylenediamine as indicated by the fact that the dibenzamide derived from them melted at 170–173° after two crystallizations. Thus, at least 70% of the diamine obtained from butadiene was the straight-chain isomer.

In another experiment, vanadium(III) sulfate was used as the reducing agent. To a mixture of 1100 ml. of acetic acid, 200 ml. of water, 77 g. of hydroxylamine hydrochloride and 27 ml. of concentrated sulfuric acid was added at 25° 480 ml. of 1.4 molar vanadium(III) sulfate with vigorous stirring over a period of 49 minutes. Concurrently, butadine (gas) was added at the rate of two liters per minute. The amines obtained were isolated by concentrating under reduced pressure, adding excess 40% sodium hydroxide, and extracting with three 1.3-lb. portions of ether and two 0.75-liter portions of methylene chloride. Distillation through a Vigreux column gave the following fractions: (1) 20.2 g. b.p. 86–100° (3 mm.), neut. equiv., 75.0; (2) 6.5 g., b.p. 100–140° (3 mm.), neut. equiv., 97.5; and (3) 8.6 g. of residue, neut. equiv., 82.7.

Redistillation of fraction 1 through a precision still gave eight cuts with refractive indices at 25° ranging from 1.4931 to 1.4995. The neutral equivalent of the first six cuts (88% of total) were 71.8 ± 0.9 (calculated for $C_8H_{16}N_2$, 70.1). The infrared spectra of the six cuts indicated that the proportion of straight-chain diamines was greatest in the high-boiling cuts.

Redistillation of fraction 2 gave four cuts with refractive indices ranging from 1.4989 to 1.5019. The neutral equivalents of these cuts were 92.0, 98.0, 97.5 and 98.3, respectively.

Anal. of Cut 3. Calcd. for $C_{12}H_{22}N_2$: C, 74.17; H, 11.40; N, 14.43; neut. equiv., 97.0. Found: C, 74.22; H, 11.57; N, 14.71; neut. equiv., 97.5.

These data indicate that fraction 2 was principally a mixture of 12-carbon diamines.

In this experiment the yield of 8-carbon diamines was about 40%; 12-carbon diamines, 15%; higher-boiling amines, 18%; and ammonia, 27%, based on the amount of vanadium(III) sulfate consumed.

III. **Reaction of Amino Radicals with Cyclohexadiene.**—To a vigorously stirred mixture of 600 ml. of methanol, 300 ml. of water, 91 g. (1.3 moles) of hydroxylamine hydro-

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(6) D. D. Coffman and E. L. Jenner, Canadian Patent 542,162, June 11, 1957. Other workers have also explored this reaction—Belgian Patent 557,730 issued to National Distillers Products Corp., May 22, 1957.

TABLE I

FRACTIONS OBTAINED FROM ETHYLENE WITH $TiCl_3$ AND NH_2OH IN AQUEOUS METHANOL

Fraction	B.p.		Wt., g.	Neut. equiv.	Analyses, %			
	°C.	Mm.			C	H	N	
1	63–76	19	1.10	118	64.33	13.59	14.78	Liquid at 0°
2	76–98	19	1.13	104	64.35	13.36	15.80	Liquid at 0°
3	98	19	0.50	75	65.05	13.97	19.12	Solid at 0°; semisolid, 25°
4	98	19	0.25	81	65.17	13.83	19.58	Solid at 0°; semisolid, 25°
5	88–112	11	1.2	91	68.89	14.0	15.88	Solid at 25°
6	112–118	11	1.5	84	67.98	13.86	17.48	Solid at 25°
7	118–111	11–4	0.5	98	69.86	13.91	14.52	Solid at 25°
8	111–90	4–1.5	1.3	100	71.53	14.02	14.63	Solid at 25°
Residue			7.5					

chloride and 80 g. (1 mole) of cyclohexadiene maintained at 25° was added over a period of 9 minutes 335 ml. (0.5 mole) of 1.5 *N* titanium(III) chloride solution. Isolation of the diamine in the usual manner gave 5.9 g. (12.3%) of a diaminobicyclohexene fraction, b.p. 131–133° (2 mm.).

Anal. Calcd. for $C_{12}H_{20}N_2$: N, 14.56; C, 74.95; H, 10.48; neut. equiv., 97.1. Found: N, 14.45; C, 74.76; H, 10.72; neut. equiv., 96.2.

Higher-boiling amines were also obtained.

IV. **Reaction of Amino Radicals with Isoprene.**—The reduction of hydroxylamine hydrochloride with titanium(III) chloride in the presence of excess isoprene was carried out under conditions similar to those used for butadiene. There were obtained several fractions (21% yield based on $TiCl_3$), b.p. 93–110° (1 mm.) with neutral equivalents varying from 83.1 to 86.4 (calculated for C_{10}-diamine, 84.0).

V. **Reaction of Amino Radicals with Cyclopentadiene.**—This reaction was carried out in a manner similar to that described for cyclohexadiene. There was obtained 8.8 g. (21.5%) of a diaminobicyclopentene fraction, b.p. 96–98° (1.1 mm.).

Anal. Calcd. for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06; neut. equiv., 82.1. Found: C, 72.57; H, 10.22; N, 17.63; neut. equiv., 82.3.

Higher-boiling amines were also obtained. A fraction, b.p. 140–145° (1.1 mm.), contained 12.7% nitrogen and was apparently a product containing more than one cyclopentene unit for each amino group.

VI. **Reaction of Amino Radicals with Ethylene.**—Reactions of ethylene were carried out in a 1.2-liter stainless steel autoclave. The products obtained depended upon the reaction conditions, solvent, and the nature of the reducing agent.

Reducing Agent, $TiCl_3$; Solvent, Acetic Acid.—To a mixture of 1100 ml. of acetic acid, 200 ml. of water, 77 g. of hydroxylamine hydrochloride, 42 ml. of concentrated hydrochloric acid and 250 g. of ethylene was added 690 ml. (1.0 mole) of titanium(III) chloride over a period of one hour at about 25°. There were obtained trace amounts of ethylamine, butylamine (2.0 g., 2.7% yield), hexylamine (1.5 g., 1.5% yield) and some higher-boiling amines not completely characterized. The amines were identified by their physical properties and by mixed melting point determinations of their phenyl isothiocyanate derivatives with authentic specimens.

Reducing Agent, $TiCl_3$; Solvent, Methanol.—In this experiment the reaction of ethylene and amino radicals was carried out essentially as given in the previous experiment except that methanol was used as the solvent instead of acetic acid. On distillation there were obtained 1.4 g. (1.9%) of butylamine and 0.5 g. (0.5%) of hexylamine. Higher boiling fractions also were obtained (see Table I). The elemental analyses and neutral equivalents of fractions 1 and 2 indicated that these fractions contained ethanolamine and octylamine. These fractions were combined and mixed with water. The water-insoluble fraction was separated and distilled, b.p. 178–180° (boiling point of octylamine, 180°).

Anal. Calcd. for $C_8H_{19}N$: N, 10.84. Found: N, 10.74.

The identification of this material as octylamine was confirmed by comparing its infrared spectrum with that of an authentic sample.

Fractions 3–8 obviously contained relatively high proportions of diamines. Octamethylenediamine was shown to be a component of fractions 5–8 by paper chromatography analysis using the method of Bremner and Kenten.[7]

Through the use of paper chromatography, it has been shown that ethylamine, butylamine, hexylamine, octylamine, ethylenediamine, tetramethylenediamine, hexamethylenediamine and octamethylenediamine are products obtained from ethylene and amino radicals.

Reducing Agent, Vanadium(III) Sulfate; Solvent, Water.—A vanadium(III) sulfate solution (1.1 liters, 1.0 mole) was added during the course of 60 minutes to a mixture of 1.67 moles of hydroxylamine hydrochloride, 8.9 moles of ethylene, 1.0 mole of hydrochloric acid and 1300 ml. of water. There was obtained ethylamine (5%), butylamine (15%), ethanolamine (38%), 4-hydroxybutylamine (18%) and about 4% of higher boiling amines. Ethylamine and butylamine were identified by their boiling points and by paper chromatographic analysis. Ethanolamine was identified by its boiling point, neutral equivalent and infrared spectrum. 4-Hydroxybutylamine was identified by its boiling point (113° (24 mm.) or 204° (atm.)(8), neutral equivalent and elemental analysis. Its infrared spectrum is also consistent with this structure.

Anal. Calcd. for $C_4H_{11}ON$: C, 53.89; H, 12.44; O, 17.95; N, 15.72; neut. equiv., 89.1. Found: C, 53.84; H, 12.48; O, 17.93(9); N, 15.82; neut. equiv., 88.5.

VII. **Reaction of Amino Radicals with 2-Butene.**—To a mixture of 1100 ml. of methanol, 200 ml. of water, 77 g. (1.1 moles) of hydroxylamine hydrochloride, 42 ml. of concentrated hydrochloric acid and 250 g. of *trans*-2-butene in an autoclave was added 590 ml. (1.0 mole) of titanium(III) chloride solution over a period of one hour at 25–30°. On distillation there were obtained 6.2 g. (8.5%) of 1-methylpropylamine, b.p. 62°, neut. equiv., 72.5 and $n^{25}D$ 1.3976 (as compared with literature values of 63°, 73.1 and 1.3950, respectively) and 8.9 g. (12.4%) of 1,2,3,4-tetramethyltetramethylenediamine (b.p. 63.5° (5 mm.)), $n^{25}D$ 1.4613.

Anal. Calcd. for $C_8H_{20}N_2$: C, 66.60; H, 13.97; N, 19.42; neut. equiv., 72.1. Found: C, 66.78; H, 14.05; N, 19.12; neut. equiv., 74.2.

The proton magnetic resonance spectrum of the diamine was consistent with the $H_2N(CHCH_3)_4NH_2$ structure.

Similar products were obtained with *cis*-2-butene.

VIII. **Reaction of Amino Radicals with Propylene.**—The reaction of propylene and amino radicals was carried out in an autoclave at room temperature in aqueous acetic acid as solvent. There was obtained approximately 21% distillable amines and 4.8% non-distillable basic residue based on the titanium(III) chloride used. A small amount (0.6%) of propylamine, identified by its boiling point 46–48° and infrared spectrum, was recovered from the ether extracts. On distillation a fraction (b.p. 115–121°, neut. equiv. 100) was obtained (yield 5%) which was probably mainly 2-methylpentylamine (calcd. neut. equiv. 101, reported[10] b.p. 64° (90 mm.) (extrapolated 120°)). Higher-boiling fractions (83° (20 mm.)–60° (1 mm.)) were also obtained (14%). These were combined and found to be only partly soluble in water. Most of the water-insoluble material distilled at 66–68° (10 mm.) (C, 71.00; H, 13.16; N, 15.18;

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(7) J. M. Bremner and R. H. Kenten, *Biochem. J.*, **49**, 651 (1951).

(8) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 1, 1946, p. 64, gives b.p. 206° (776 mm.).

(9) Modified Unterzaucher procedure.

(10) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **98**, 1 (1932).

neut. equiv., 92.8) and was apparently a mixture of mono- and diamines. The water-soluble material for the most part distilled at 67–69° (10 mm.) (C, 66.98; H, 13.29; N, 19.99; neut. equiv., 74.7; $n^{25}D$ 1.4533) and was apparently a mixture of C_6-diamines and C_9-monoamines.

IX. Reactions of Amino Radicals with Isobutylene.—The experiment was carried out under the conditions described for propylene. The total yield of amines was about 16% based on the titanous chloride used. One of the products was isobutylamine (5%) identified by its boiling point (70°) and by a comparison of its phenyl isothiocyanate derivative (m.p. 78–80°) with an authentic sample. A complex mixture of higher-boiling amines was also obtained. One fraction (1%), b.p. 173–174°, analyzed for a C_8-diamine.

Anal. Calcd. for $C_8H_{20}N_2$: C, 66.60; H, 13.97; N, 19.42; neut. equiv., 72.1. Found: C, 66.96; H, 13.48; N, 20.01; neut. equiv., 72.7.

X. Reaction of Amino Radicals with 1-Hexene.—Reaction of 1-hexene and amino radicals at room temperature in aqueous acetic acid as solvent gave 0.5 g. (1.0%) of hexylamine and 5 g. (10%) of a product distilling at 106–111° (2 mm.). This product appears to be 2,3-dibutyltetramethylenediamine, but complete structure proof is not available.

Anal. Calcd. for $C_{12}H_{28}N_2$: C, 71.93; H, 14.08; N, 13.99; mol. wt., 200.4; neut. equiv., 100.2. Found: C, 72.01; H, 13.58; N, 14.5; mol. wt., 202; neut. equiv., 103.0.

There was also obtained about 4.1 g. of amine which distilled at 75–80° (0.001 mm.).

XI. Reaction of Amino Radicals with Tetramethylethylene.—Under the conditions used for 1-hexene, tetramethylethylene was found to react with amino radicals to give two main products: (1) 1,1,2-trimethylpropylamine (5% yield), b.p. 103–105°, $n^{25}D$ 1.4148, neut. equiv. 103.9; (2) 2-hydroxy-1,1,2-trimethylpropylamine (4% yield), b.p. 163–165°, $n^{25}D$ 1.4480, neut. equiv. 118.7. The 1,1,2-trimethylpropylamine was identified by comparison with the 6-carbon amines prepared from 2,3-dimethyl-2-nitrobutane and pinacolone oxime. The following comparison clearly indicates the structure of the amine obtained:

	Product (1)	$H_2NC(CH_3)_2$-$CH(CH_3)_2$	$H_2NCH(CH_3)$-$C(CH_3)_3$
B.p., °C.	103–105	102.9	103.0
M.p., °C., of C_6H_5NCS der.	103.5–104.5	104.5–105.5	120–121
	(No depression on mixing)		

The higher-boiling alkanolamine was identified by comparison with an authentic sample obtained by treating tetramethylethylene oxide with ammonia.

	Product (2)	$H_2NC(CH_3)_2C$-$(CH_3)_2OH$
B.p., °C. (mm.)	112–114 (165)	112 (165)
$n^{25}D$	1.4480	1.4480
Neut. equiv.	118.7	117.19
M.p., °C., of C_6H_5NCS der.	139–141	140–141
	(No depression on mixing)	

Anal. Calcd. for $C_6H_{15}ON$: C, 61.49; H, 12.90; N, 11.95. Found: C, 61.72; H, 12.85; N, 12.34.

XII. Reaction of Amino Radicals with Benzene.—Benzene and amino radicals reacted at room temperature in an aqueous acetic acid reaction medium to form an unstable amine in 30% yield (neut. equiv. of crude product 95 *vs.* 94 for a 1:1 benzene/amino radical adduct). An attempted distillation resulted in extensive decomposition with the formation of biphenyl.

A mixture of 10.0 g. (0.1 equivalent) of crude, unstable amine, 275 ml. of absolute ethyl alcohol and 0.5 g. of platinum oxide was shaken with hydrogen under 2–3 atmospheres pressure. Hydrogenation proceeded rapidly with about 0.19 mole of hydrogen being absorbed. Much ammonia (at least 30% yield) was formed along with (1) 0.03 g. of aniline; (2) 1.5 g. of aminobicyclohexyl, b.p. 120–128° (8 mm.); and (3) 0.23 g. of diaminobicyclohexyl, b.p. 120 (<1 mm.). Aniline was identified by its ultraviolet spectrum; aminobicyclohexyl by its neutral equivalent, boiling point and proton magnetic resonance spectrum; and diaminobicyclohexyl by its neutral equivalent and nitrogen analysis (Calcd. for $C_{12}H_{22}N_2$: N, 14.28; Found: N, 14.23). The position of the amino groups has not been determined.

XIII. Reaction of Amino Radicals with Toluene.—Toluene reacted with amino radicals under the conditions used for benzene to give about a 30% yield of an unstable amine. It had a neutral equivalent of 117 as compared with 108 for a 1:1 adduct. The proton magnetic resonance spectrum of the crude product indicated that 15–20% of the hydrogens were aromatic and the remainder olefinic. A low yield of *p*-toluidine was recovered by distillation. One of the decomposition products was presumably ditolyl.

XIV. Reaction of Methylamino Radicals with Butadiene.—When N-methylhydroxylamine, prepared by the zinc dust–ammonium chloride reduction of nitromethane, was substituted for hydroxylamine in reaction with butadiene using an aqueous methanolic solution at −5° there was obtained a 39% yield of N,N′-dimethyldiaminoöctadienes, b.p. 77–93° (4 mm.), neut. equiv. 84.8 (calcd. for $C_{10}H_{20}N_2$, 84).

XV. Reactivity of Amino Radicals toward Certain Solvents (Table II).—A method similar to that of Davis, Evans and Higginson[1] was employed. Excess titanium(III) sulfate solution was added dropwise to a vigorously stirred solution (40 ml.) containing 3.3 ml. of sulfuric acid and 0.010 mole of hydroxylamine hydrochloride in the indicated solvent. The excess Ti^{3+} was titrated with standard $FeCl_3$ solution. Qualitative tests for carbonyl compounds were made on distilled samples using 2,4-dinitrophenylhydrazine reagent and ammonia was determined by the Kjeldahl procedure.

TABLE II

REACTIONS OF AMINO RADICALS WITH SOLVENTS

Solvent (ratio by vol.)	Consumption fraction (Ti^{3+}/NH_2OH)	NH_2OH converted to NH_3, %
Water	2.0	100
Water satd. with butadiene	1.05	8
Methanol–water (1:8)[a]	0.9	100
Ethanol–water (1:8)[a]	.6	95
Isopropyl alc.–water (1:8)	.4	99
t-Butyl alcohol–water (1:8)[a]	1.5	93
Acetone–water (1:3)	0.7	
Dimethylformamide–water (1:3)	1.4	
Acetic acid–water (1:3)	2.0	100

[a] These three experiments were tested for carbonyl compounds; the methanol and ethanol runs gave strong tests; the *t*-butyl alcohol gave a weak test.

The amount of formaldehyde formed by oxidation of methanol was determined as follows: To a well-stirred mixture comprising 36 ml. of water, 4 ml. of sulfuric acid, 5 ml. of methanol and 0.010 mole of hydroxylamine was added 22 ml. of titanium(III) sulfate solution (0.90 *M*) over a period of 9 minutes. Excess titanium(III) sulfate was titrated with 1.0 *M* ferric chloride. The consumption of titanium(III) sulfate was 0.009 mole. Formaldehyde removed from the reaction mixture by distillation was assayed by the sodium sulfite volumetric method. The yield of formaldehyde was 27% (0.027 mole) based on the hydroxylamine used.

XVI. Reaction of Amino Radicals with Bromide Ions.—Chloride ions do not react with amino radicals under the conditions employed in this work. However, bromide ions do react with amino radicals as indicated by the following experiments. To a mixture of 10.0 ml. of 1.0 molar aqueous hydroxylamine hydrochloride solution, 5 ml. of concentrated hydrochloric acid and 25 ml. of water saturated with butadiene, was added 6.5 ml. of 1.78 molar titanium(III) chloride solution over a period of about 4 minutes. Back titration of the unreacted titanium(III) chloride with excess standard ferric alum solution indicated that 1.05 moles of titanium(III) chloride was consumed for each mole of hydroxylamine consumed, which corresponds to a yield of amines of about 95%. No insoluble products formed during the reaction. On the other hand, when this experiment was repeated with the addition of 2.1 g. of sodium bromide to the reaction mixture prior to the addition of titanium(III) chloride, an oily, sharp-smelling product separated during the reaction. This water-insoluble product was (undoubtedly) a mixture of aliphatic (allylic) bromides[11] formed by the addition of bromine atoms, generated by oxidation of bromine ions with amino radicals, to butadiene. The molar ratio of titanium(III) chloride consumed to hydroxylamine consumed was 1.64, indicating that about 36% of the bromine atoms generated reacted with butadiene and 64% with titanium(III) ions.

WILMINGTON, DEL.

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[11] Products of this type will be described in a forthcoming paper in this series.

[CONTRIBUTION FROM THE AMERICAN CYANAMID CO., RESEARCH DIVISION]

The Oxidation of Pinacol by Ceric Sulfate

BY G. MINO, S. KAIZERMAN AND E. RASMUSSEN

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The oxidation of pinacol (2,3-dimethylbutandiol-2,3) by ceric sulfate was studied at 25°. The reaction is first order with respect to ceric ion and pinacol. No evidence of complexing between the sulfatocerate species and the glycol was found. The data show that one molecule of acetone is formed per ceric ion consumed. In the presence of acrylamide one molecule of acetone is formed per two ceric ions consumed. To explain the data a mechanism is proposed whereby the primary radicals are captured by the acrylamide, the efficiency of capture being of the order of 100%, and the polymer radicals are terminated by ceric ion. The data also show that the carbon-to-carbon bond of the 1,2-glycol is split before the free radical is captured. The activation energy for the over-all reaction was found to be 22.5 kcal./mole.

Introduction

It has been shown that the oxidation of 1,2-glycols by ceric salts[1,2] proceeds through the disproportionation of coördination complexes. During the disproportionation of these complexes, free radicals are formed which initiate vinyl polymerization.[3]

The purpose of this work was to study the oxidation of 1,2-glycols by ceric ion in the presence of a free radical scavenger. It was thought that the stoichiometry of the reaction, determined in the presence or in the absence of a free radical scavenger, would yield useful information about the capture of the free radicals by the monomer and about the oxidation of the free radicals by ceric ion.

Pinacol (2,3-dimethylbutandiol-2,3) was used because upon oxidation it produces acetone, which is very resistant to further oxidation by ceric ion.

Ceric sulfate was chosen because it oxidizes pinacol at a measurable rate at room temperature, while ceric nitrate oxidizes it almost instantaneously even at 0°.

Experimental

1. **Material Used.**—Commercial pinacol was distilled at atmospheric pressure, b.p. 172°.

Anal. Found: C, 61.19; H, 11.64; O, 27.25. Calcd.: C, 60.98; H, 11.94; O, 27.07.

The ceric ammonium sulfate, $(NH_4)_4[Ce(SO_4)_4]\cdot 2H_2O$, reagent grade, from G. Frederick Smith Chemical Co., was dissolved in 1 *N* sulfuric acid and the stock solution, 0.1 *M* in ceric sulfate, was used to prepare the recipes.

Commercial acrylamide, from American Cyanamid Co., was sublimed at 60° under reduced pressure (0.05 mm.).

2. **Determination of the Rate of Reaction.**—Ten ml. of water was added to a 100-ml. volumetric flask followed by 10 ml. of *M* sodium sulfate, 20 ml. of *N* sulfuric acid and the required amount of pinacol solution, to give the desired final concentration and a total volume of 90 ml. The flask was thermostated at 25 ± 0.05° for 0.5 hour; 10 ml. of ceric sulfate solution, 0.1 *M* in *N* sulfuric acid, kept at 25°, was then added. Ten-ml. samples were withdrawn at recorded times, quenched in an excess of 0.01 *N* ferrous ammonium sulfate in 0.5 *N* sulfuric acid, and the excess ferrous salt was back titrated with 0.01 *M* ceric sulfate, using *o*-phenanthroline as an indicator. All other experiments were carried out in a similar manner, varying the concentration of the reactants as required. Rate determinations in the presence of acrylamide were carried out in screw-capped bottles, under nitrogen.

3. **Determination of the Acetone Formed.**—Acetone was identified as the reaction product by isolation of its 2,4-dinitrophenylhydrazone and determined spectrophotometrically by the method of Behre and Benedict.[4] Ten-ml. samples were withdrawn from the reaction flask and quenched with 0.5 ml. of saturated aqueous KOH. The hydroxides of cerium were filtered off and 2 ml. of the filtrate added to 1 ml. of salicylic aldehyde in 100-ml. volumetric flasks. After adding 15 ml. of saturated aqueous KOH, the samples were allowed to stand for 20 minutes and then brought to volume. If the red color developed was too intense, the samples were diluted further with distilled water. The optical densities of the solutions were determined at 520 mμ on a G. E. spectrophotometer, using a 1-cm. cell.

The concentration of acetone in the samples was read from a calibration curve obtained by plotting the optical densities of reference solutions, containing known amounts of acetone *vs.* the concentration. The reference solutions contained the same amounts of pinacol, cerous salts, sodium sulfate and sulfuric acid as the samples under examination. When acrylamide was used as a free radical scavenger (see Table V), a new calibration curve was prepared from reference solutions containing the same amount of acrylamide as the samples to be analyzed.

Data and Discussion

The oxidation of pinacol was studied at 25°. At constant *p*H and in the presence of an excess of glycol, the rate of the reaction is first order with respect to the concentration of total ceric ion ($\mathrm{Ce^{IV}}$) and can, therefore, be represented by

$$-\,d(\mathrm{Ce^{IV}})/dt = K'(\mathrm{Ce^{IV}})$$

The rate of the reaction was found to be the same in nitrogen and in air . The values of K', the over-all first-order constant, reported in the tables, were calculated from the slopes of the plots log ($\mathrm{Ce^{IV}}$) *vs.* time.

The dependence of K' on the pinacol concentration was studied at one hydrogen ion and sulfate ion concentration only (*p*H 0.97, $(SO_4^{=})_T = 0.29$ mole per liter). Figure 1 shows that K' varies linearly with the pinacol concentration. From the slopes of this plot the value of the second-order

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