63–65°); ir (KBr) 1628 cm^{-1} (s); nmr (CCl_4) δ 2.01 (s, 3 H), 3.97–4.26 (m, 9 H), 4.53 (s, 1 H), 5.02 (s, 1 H).

Immediately after this fraction, 560 mg of polyvinylferrocene (**5**) was eluted: mol wt (gpc) ~1800; ir identical with that of an authentic sample obtained by radical polymerization of vinylferrocene.[14,15]

Further elution with 1:3 benzene–petroleum ether afforded 150 mg of a mixture of the two isomers of triferrocenylbenzene, **1** and **2** (roughly in the same amount by nmr analysis).

Continued elution with 1:1 benzene–petroleum ether afforded 1.90 g of ethyl ferrocenoate (**4**), which was recrystallized from ethanol–water: mp 62–63° (lit. mp 61–62°,[11] 63–64°[16]); ir (KBr) 1700 cm^{-1} (s); mass spectrum (70 eV) *m/e* (assignment and rel intensity) 258 (M^+, 100), 229 ($M^+ - C_2H_5$, 99), 213 ($M^+ - C_2H_5O$, 10), 185 ($C_{10}H_9Fe^+$, 11), 56 (Fe^+, 85); nmr (CCl_4) δ 1.32 (t, 3 H), 4.1–4.35 (m, 9 H), 4.70 (m, 2 H).

Elution with pure benzene afforded 1.01 g of acetylferrocene followed by 200 mg of dimer **3**.

(14) F. S. Arimoto and A. C. Haven, *J. Amer. Chem. Soc.*, **77**, 6295 (1955).

(15) Y. Sasaki, L. L. Walker, E. L. Hurst, and C. U. Pittman, Jr., *J. Polym. Sci.*, **11**, 1213 (1973).

(16) R. F. Schaaf, *J. Org. Chem.*, **27**, 107 (1962).

Further elution with 1:2 benzene–diethyl ether afforded 200 mg of hydroxyl-bearing polymeric species **7**: mol wt (gpc) ~2900; ir (KBr) 3400 (broad), 3070 (s), 2890 (s), 1450 (s), 1370 (s), 1105 (s), 1000 (s), 820 cm^{-1} (s); nmr ($CDCl_3$) δ ~4.2 (very broad, ~9 H), 1.9 (very broad, ~3 H).

Treatment of Dimer 3 with Triethyl Orthoformate in Ethanol in the Presence of a Small Amount of *p*-Toluenesulfonic Acid.—Dimer **3** (1.00 g, 2.28 mmol), triethyl orthoformate (1.3 g, 9 mmol), and *p*-toluenesulfonic acid (50 mg, 0.26 mmol) were dissolved in 10 ml of dry ethanol and stirred well at room temperature. Tlc studies were conducted from time to time. Even after 2 weeks, no reaction occurs to give any of compounds **1**–**7**.

Acknowledgments.—This work was supported in part by the Air Force Cambridge Laboratories under Contract No. F19628-71-C-0107. The work reported here does not necessarily reflect endorsement by the Air Force. Partial support was provided by the Office of Naval Research.

Registry No.—**1**, 39324-45-3; **3**, 39336-59-9; **4**, 1273-91-2; **6**, 33362-30-0; acetylferrocene, 1271-55-2; triethyl orthoformate, 122-51-0.

Fused Organic Salts. VII.[1] The System Tetra-*n*-pentylammonium Nitrate–Silver Nitrate. Melt Stability. The Silver Nitrate–Carbon Tetrachloride Reaction

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Received April 12, 1973

Tetra-*n*-pentylammonium nitrate (fp 113.9°)–silver nitrate (fp 210°) is a simple eutectic system with eutectic temperature 41.7° and eutectic composition 42.2 ± 0.5 mol % $AgNO_3$. While pure tetra-*n*-penytlammonium nitrate gives 1-pentyl nitrate and tripentylamine on pyrolysis at 275°, $AgNO_3$–R_4NNO_3 mixtures yield in addition dipentylnitrosamine. This oxidation of tertiary amine by $AgNO_3$ is observable also in protic and aprotic solvents. Ag metal is formed and the tertiary iminium cation and tertiary amide are thought to be intermediates. The $AgNO_3$–CCl_4 reaction, which is very slow in ethanol but very rapid with $AgNO_3$ adsorbed on silicic acid, proves also to be very slow in molten $AgNO_3$–R_4NNO_3. Consequently the difference in reactivity in the first two media cannot be attributed to deactivation by ion solvation, and the high reactivity of $AgNO_3$/silicic acid must be a surface-chemical phenomenon.

Results and Discussion

Phase Diagram.—Tetra-*n*-pentylammonium nitrate–silver nitrate displays a simple eutectic diagram (Figure 1) with a remarkably low eutectic temperature (41.7 ± 0.5°). The eutectic melt contains 42.4 ± 0.5 mol % (25.7 wt %) of silver nitrate. The availability of such melts containing high concentrations of unsolvated silver ion at moderate temperatures suggests a variety of chemical applications. Here we report on stability relationships in these melts and one test of the electrophilic reactivity of Ag^+ in Ag^+, R_4N^+/NO_3^-.

Stability of the Melt.—While pure liquid $R_4N^+NO_3^-$ is more stable than its analogs with more nucleophilic anions, slow decomposition is known to occur at 140°.[2] This reaction could take either of two paths: nucleophilic displacement (eq 1) or elimination (eq 2).[3] Application of the vacuum pyrolysis technique which provided clean-cut results for the halides[1a] produced the result shown in Table I. Only reaction 1 is important.

$$(n\text{-}C_5H_{11})_4N^+NO_3^- \rightarrow CH_3(CH_2)_3CH_2ONO_2 + (n\text{-}C_5H_{11})_3N \quad (1)$$

$$(n\text{-}C_5H_{11})_4N^+NO_3^- \rightarrow CH_3(CH_2)_2CH{=}CH_2 + (n\text{-}C_5H_{11})_3N + HNO_3 \quad (2)$$

The behavior of R_4N^+, Ag^+/NO_3^- mixtures is expected to be similar, with possible secondary reactions of the products of eq 1 with Ag^+. The observations (Table I) are indeed similar, but the yield of tripentylamine is reduced and some dipentylnitrososamine appears. The latter was shown to result from reaction of tripentylamine with $AgNO_3$.

This reaction takes the course shown in Table II and eq 3. Oxidation of tertiary amines by Ag^+ has

$$2AgNO_3 + (C_5H_{11})_3N = 2Ag + (C_5H_{11})_2NN{=}O + HNO_3 + CH_3(CH_2)_3COOH \quad (3)$$

apparently never been reported, though other oxidants (ClO_2, MnO_2, $Hg(OAc)_2$, $KMnO_4$) are known to produce the enamine or its conjugate acid.[4] We in-

(1) (a) Part VI: J. E. Gordon and P. Varughese, *Chem. Commun.*, 1160 (1971). (b) Part V: J. E. Gordon, J. E. Selwyn, and R. L. Thorne, *J. Org. Chem.*, **31**, 1925 (1966). (c) Part IV: J. E. Gordon, *J. Amer. Chem. Soc.*, **87**, 4347 (1965).

(2) J. E. Gordon, *J. Org. Chem.*, **30**, 2760 (1965).

(3) J. E. Gordon in "Techniques and Methods of Organic and Organometallic Chemistry," D. B. Denney, Ed., Marcel Dekker, New York, N. Y., 1969, p 78.

(4) (a) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, p 49; (b) L. A. Hull, *et al.*, *J. Amer. Chem. Soc.*, **89**, 1163 (1967).

TABLE I

PRODUCTS OF VACUUM PYROLYSIS OF MOLTEN NITRATES[a]

Reactants	Temp, °C	Products, % Tripentylamine	Pentyl nitrate	1-Pentene	Dipentylnitrosamine
$(n\text{-}C_5H_{11})_4N^+NO_3^-$	250–280	93	68	3	Trace
$(n\text{-}C_5H_{11})_4N^+NO_3^-$–$AgNO_3$[b]	250–280	80	79	4	3
$(n\text{-}C_5H_{11})_3NH^+NO_3^-$	150[c]	49			13

[a] 0.001 Torr. [b] 35 mol % $AgNO_3$. [c] In sealed ampoule.

TABLE II

PRODUCTS FROM $(C_5H_{11})_3N$ AND $AgNO_3$[a]

Solvent	Temp, °C	Products, % $(C_5H_{11})_3N$	$(C_5H_{11})_2NN{=}O$
Neat	110	2	55
$C_6H_5NO_2$	110	4	68
t-C_4H_9OH	83	21	10
R_4N^+, Ag^+/NO_3^-[b]	110	c	54

[a] Reaction time, 24 hr. Metallic silver and valeric acid also observed; see Experimental Section. [b] 35 mol % $AgNO_3$. [c] Not determined.

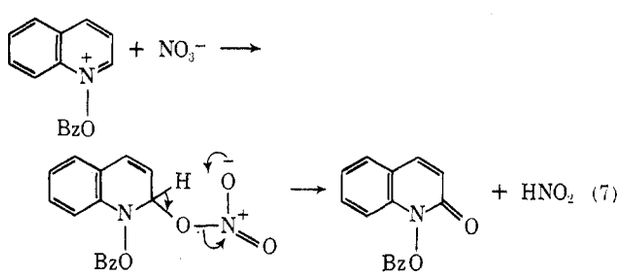
terpret the course of this reaction as eq 4 + eq 5 + eq 6 = eq 3. Nucleophilic addition of nitrate ion to the

$$2Ag^+ + (C_5H_{11})_3N \longrightarrow 2Ag + (C_5H_{11})_2N^+{=}CH(CH_2)_3CH_3 + H^+ \quad (4)$$

$$(C_5H_{11})_2N^+{=}CH(CH_2)_3CH_3 + NO_3^- \longrightarrow (C_5H_{11})_2NCH(CH_2)_3CH_3 \longrightarrow \underset{ONO_2}{(C_5H_{11})_2NCH(CH_2)_3CH_3} \longrightarrow (C_5H_{11})_2N\overset{O}{\overset{\|}{C}}(CH_2)_3CH_3 + HNO_2 \quad (5)$$

$$(C_5H_{11})_2N\overset{O}{\overset{\|}{C}}(CH_2)_3CH_3 + H^+ + HNO_2 \longrightarrow (C_5H_{11})_2N^+CO(CH_2)_3CH_3 + H_2O \longrightarrow \underset{N=O}{(C_5H_{11})_2NN{=}O} + HOOC(CH_2)_3CH_3 + H^+ \quad (6)$$

iminium salt, followed by loss of nitrous acid (eq 5), finds a close analogy in the reaction of quinoline *N*-oxide with benzoyl nitrate (eq 7).[5] The nitrosation of



tertiary amides (eq 6) is known[6] to produce the nitrosamine.

The R_3N–$AgNO_3$ reaction was shown to occur in molten R_4NNO_3 medium (Table II) and we consequently attribute the appearance of dipentylnitrosamine in the pyrolysis of Ag^+, R_4N^+/NO_3^- to eq 1 followed by eq 3.

The $AgNO_3$–CCl_4 Reaction in Molten R_4N^+, Ag^+/NO_3^-.—Carbon tetrachloride reacts with $AgNO_3$ slowly in refluxing ethanol, but rapidly with $AgNO_3$ on silicic acid at room temperature.[7] A nitrating agent results, and in the presence of an aromatic substrate processes 8 (interpreted as the sum of eq 10–12 and half of 15) and 9 (interpreted as the sum of eq 10–15) proceed simultaneously.

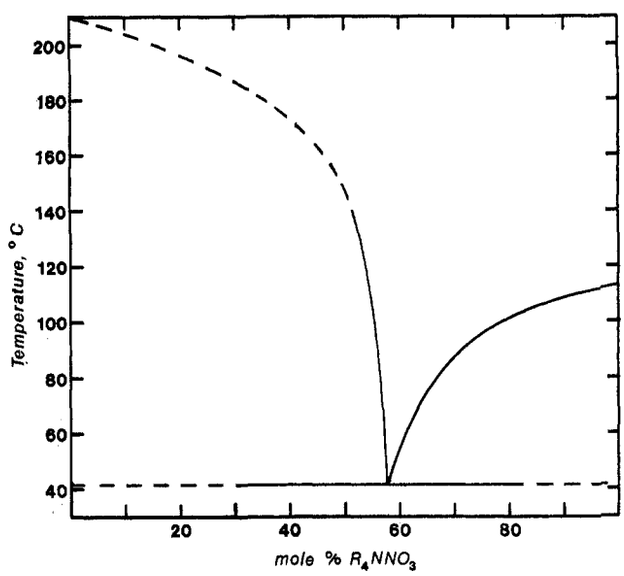


Figure 1.—Phase diagram for the system $AgNO_3$–$(n\text{-}C_5H_{11})_4NNO_3$. The dotted portions are somewhat less certain (liquidus, due to decomposition; solidus, due to difficulty in visual identification of molten eutectic at the composition extremes).

$$CCl_4 + 2AgNO_3 + ArH = 2AgCl + COCl_2 + ArNO_2 + HNO \quad (8)$$

$$CCl_4 + 4AgNO_3 + 2ArH = 4AgCl + 2ArNO_2 + CO_2 + 2HNO_3 \quad (9)$$

$$CCl_4 + AgNO_3 \longrightarrow CCl_3ONO_2 + AgCl \quad (10)$$

$$CCl_3ONO_2 \longrightarrow COCl_2 + NO_2Cl \quad (11)$$

$$NO_2Cl + AgNO_3 \longrightarrow N_2O_5 + AgCl \quad (12)$$

$$COCl_2 + 2AgNO_3 \longrightarrow 2AgCl + CO(ONO_2)_2 \quad (13)$$

$$CO(ONO_2)_2 \longrightarrow CO_2 + N_2O_5 \quad (14)$$

$$2ArH + 2N_2O_5 \longrightarrow 2ArNO_2 + 2HNO_3 \quad (15)$$

In molten R_4N^+, Ag^+/NO_3^- at 110° the reaction of CCl_4 differs considerably from this pattern. No phosgene is detectable, added ArH is not nitrated, and deposition of AgCl is slow. From the very much lower level of reactivity in the melt we conclude that NO_3^- of maximum nucleophilicity[1a] and unsolvated, presumably strongly electrophilic, Ag^+ are insufficient to make the displacement reaction 10 go rapidly. One must therefore look to the surface chemistry of $AgNO_3$/silicic acid for an understanding of the great reactivity with CCl_4.

(5) A. R. Katritzky and J. M. Lagowski, "Chemistry of the Heterocyclic *N*-Oxides," Academic Press, New York, N. Y., 1971, pp 247, 292.

(6) W. Lijinsky, E. Conrad, and R. Van de Bogart, *Nature (London)*, **239**, 165 (1972).

(7) J. E. Gordon, *J. Org. Chem.*, **35**, 2722 (1970).

The principal product from CCl_4–$AgNO_3$ in molten R_4NNO_3 is in fact $R_2NN{=}O$ (Table III), and we attribute its formation to interception of the nitrating agent formed from CCl_4–$AgNO_3$ by the tripentylamine from decomposition of R_4NNO_3. This is summarized by eq 16, which is the sum of eq 10–14, 2 × eq 1 and

TABLE III

PRODUCTS FROM CCl_4 AND $AgNO_3$ IN MOLTEN TETRAPENTYLAMMONIUM NITRATE[a]

Reactants, mmol				Products, mmol	
$AgNO_3$	R_4NNO_3	CCl_4	R_3N	$R_2NN{=}O$	1-Pentene
2.54	4.64	1.53		0.074	
2.52	4.65	1.53	0.171	0.200	
2.52	4.66		0.171	0.093	Trace

[a] 110° for 24 hr.

$$CCl_4 + 4AgNO_3 + 2(C_5H_{11})_4NNO_3 = 4AgCl + CO_2 + 2C_5H_{11}ONO_2 + 2(C_5H_{11})_2NNO + 2C_4H_9CHO + 2HNO_3 \quad (16)$$

2 × eq 17. The nitration of tertiary amines by tetranitromethane is known to give the secondary nitrosamine,[8] and we have confirmed that nitration by HNO_3 does also by studying the pyrolysis of tripentylammonium nitrate (Table I).[9] The reaction can be rationalized by analogy with the nitrosation of tertiary amines[12] and the nitration by $C(NO_2)_4$[13] as eq 18–21,

$$(C_5H_{11})_3N + N_2O_5 = (\text{or } HNO_3 + H^+) \longrightarrow (C_5H_{11})_2NN{=}O + C_4H_9CHO + \underset{(\text{or } H_2O)}{HNO_3} \quad (17)$$

$$(C_5H_{11})_3N + N_2O_5 \text{ (or } HNO_3 + H^+) \longrightarrow (C_5H_{11})_3N^+NO_2 + NO_3^- \text{ (or } H_2O) \quad (18)$$

$$(C_5H_{11})_3N^+NO_2 \longrightarrow (C_5H_{11})_2N^+{=}CHC_4H_9 + HNO_2 \quad (19)$$

$$(C_5H_{11})_2N^+{=}CHC_4H_9 + H_2O \longrightarrow (C_5H_{11})_2NH + C_4H_9CHO + H^+ \quad (20)$$

$$(C_5H_{11})_2NH + HNO_2 \longrightarrow (C_5H_{11})_2NN{=}O + H_2O \quad (21)$$

whose sum is eq 17. The yield of dipentylnitrosamine, based on $AgNO_3$ according to eq 16, is 12%. In the presence of added tripentylamine the production of nitrosamine rises by 0.126 mmol, a 74% yield based on R_3N. However, up to 0.093 mmol (final entry, Table III) arises from the $AgNO_3$–R_3N reaction (eq 3), and the remainder, $\geq$0.033 mmol, is due to eq 17. This partitioning of added R_3N in comparable amounts through the two pathways to $R_2NN{=}O$ probably also occurs with the R_3N arising from R_4NNO_3.

Experimental Section

General.—Tetra-*n*-pentylammonium nitrate was prepared according to Gordon,[1c] mp 113.5–114° (lit.[1c] 113.9°). 1-Pentyl nitrate, prepared according to Ferris, *et al.*,[14] was distilled at 20 Torr; the material collected at 59–60° was used after verification of identity by ir and nmr. Di-*n*-pentylnitrosamine was prepared by the procedure of Carroll and Wright[15] and distilled through a Vigreux column, bp 83–83.5° (0.45 Torr) [lit.[16] 146° (12 Torr)]. Ir and nmr [δ 0.9 (t, 6 H, J = 5 Hz, CH_3), *ca.* 1.3 (m, 12 H, CCH_2C), 3.58 (t, 2 H, J = 7 Hz, cis CH_2N), and 4.08 (t, 2 H, J = 7 Hz, trans CH_2N)] spectra were consistent with the structure and literature reports.[17,18] The mass spectrum (70 eV) showed *m/e* (rel intensity) 186 (M^+, 3), 169 (11), 129 (5), 128 (19), 113 (15), 100 (10), 98 (37), 84 (13), 71 (18), 58 (22), 57 (10), 44 (38), 43 (100), 42 (25), 41 (47), 39 (19), 30 (15), 29 (26), 27 (26).

Anal. Calcd for $C_{10}H_{22}N_2O$: C, 64.47; H, 11.90; N, 15.04. Found: C, 64.36; H, 11.99; N, 15.25.

Tri-*n*-pentylamine was Distillation Products Industries White Label. Solvents were reagent grade materials, redistilled before use. Silver nitrate was Baker Analyzed reagent grade.

Nmr spectra were obtained using a Varian A-60 instrument; mass spectra used a GEC-AEI MS-12 spectrometer. Melting points were determined by hot-stage microscopy and were corrected. Analyses were performed by Galbraith Laboratories, Inc.

Phase Diagram.—The form of the diagram and the eutectic temperature (41.4 ± 0.5°) were determined by observation of the Kofler contact preparation[19] on a Reichert–Kofler RCH-4065 hot-stage microscope. The liquidus curve was fixed by hot-stage observations of the temperature of last-crystal disappearance on thoroughly ground mixtures of known composition prepared using a microbalance. Visual identification of the excess component after eutectic fusion allowed convergence on the eutectic composition, which was fixed by this method at 42.3 ± 0.5 mol % $AgNO_3$. A second determination of the eutectic composition was made by elemental analysis of the liquid eutectic obtained in the following manner. $AgNO_3$-rich melts were seeded with $AgNO_3$, cooled slowly to *ca.* 42°, and placed in a constant-temperature bath at the eutectic temperature. Liquid samples were withdrawn and analyzed as equilibrium was established over several days, with the results shown in Table IV. The limiting composition obtained from the carbon analyses is in excellent agreement with that obtained by hot-stage microscopy. As expected,[20] the hydrogen determinations were confirmatory but less precise. The liquidus curve is unreliable beyond *ca.* 50 mol % $AgNO_3$ ($\gtrsim$150°) due to evident decomposition on the hot stage. There is evidence of incomplete liquid–liquid miscibility just above the liquidus in the vicinity of 70 mol % $AgNO_3$, but this may be an artifact produced by decomposition.

TABLE IV

COMPOSITION OF THE (n-$C_5H_{11})_4NNO_3$–$AgNO_3$ EUTECTIC LIQUID

Time, hr	Wt % C	Mol % $AgNO_3$	Wt % H	Mol % $AgNO_3$
45	47.00	46.9	8.74	45.7
65	49.23	42.9	9.13	41.8
90	49.91	41.7	9.43	38.5
115	49.33	42.8	9.47	38.2
		Mean 42.5 ± 0.5[a]		Mean 39.5 ± 1.6[a]

[a] Last three values.

Analytical Procedure.—Vacuum pyrolysates recovered from cold traps were transferred with dioxane and made up to 5.0 or 10.0 ml in volumetric flasks (runs of Table I). Products of reactions conducted in ampoules (runs of Table III) were triturated with dioxane or ethyl ether (in which the quaternary salts are insoluble) and filtered; filtrate and washings were made up to 10.0 ml in volumetric flasks.

These solutions were chromatographed on a 5 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb W, manually programmed between 90 and 190° using a Varian 90-P chromatograph with thermal conductivity detection. Peak areas from duplicate 25-μl samples were planimetrically compared with those from standard solutions chromatographed before and after the unknown. The analytical precision was ±0.3%, the detection limit for dipentylnitrosamine, 3 × 10^{-4} mmol/ml.

(8) E. Schmidt and H. Fischer, *Ber.*, **53**, 1537 (1920).

(9) Nitration of R_3N is also said to form the nitramine, R_2NNO_2;[10] this may result from oxidation of R_2NNO by HNO_3.[11]

(10) Reference 4a, p 33.

(11) F. Reverdin, *Bull. Soc. Chim. Fr.*, [4] **9**, 43 (1911).

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(15) K. K. Carroll and G. F. Wright, *Can. J. Res. Sect. B*, **26**, 271 (1948).

(16) H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *J. Amer. Chem. Soc.*, **77**, 790 (1955).

(17) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

(18) G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, **86**, 4373 (1964).

(19) L. Kofler and A. Kofler, "Thermo-Mikro-Methoden," Verlag-Chemie, Weinheim, 1954.

(20) F. W. Power, *Mikrochemie*, **22**, 263 (1937).

Vacuum Pyrolyses.—Samples (0.1 mmol) weighed into Pyrex boats were placed in a horizontal Pyrex pyrolysis tube whose entrance was then sealed off and whose exit led to a U-tube and thence to a vacuum line, the unit being formed from a single piece of glass. The system was pumped out to 10^{-3} Torr, the U-tube immersed in liquid N_2, and the pyrolysis tube heated in an air bath at 250° for 1 hr followed by 30–45 min at 270–280°. The U-tube trap was then sealed off, removed, warmed to 0°, and opened.

Reaction of $AgNO_3$–R_4NNO_3 with Carbon Tetrachloride.—Silver nitrate and tetrapentylammonium nitrate were weighed into a 5-ml ampoule and the mixture was protected from atmospheric moisture and heated at 100–110° for 24 hr to produce a homogeneous melt. CCl_4 and any other additives were added to the cooled mixture *via* a microliter syringe, and the ampoule was sealed, heated under the conditions specified in the tables, chilled, and opened.

Identification of dipentylnitrosamine in a typical product was accomplished by triturating with ether and filtering off AgCl, $AgNO_3$, and R_4NNO_3. Evaporation of the filtrate left a yellow oil whose gc retention time, nmr and mass spectra were those of authentic dipentylnitrosamine. The ir spectrum was that of dipentylnitrosamine plus bands at 3500–2200, 1720, and 945 cm^{-1} attributable to valeric acid. Gas chromatographic evidence for both valeraldehyde and valeric acid was obtained but irreproducibility prevented quantitation.

Pyrolysis of Tripentylammonium Nitrate.—A solution of 1.001 g (4.41 mmol) of tripentylamine in 40 ml of ethanol was treated with 1.04 ml of 5.03 *N* nitric acid (5.23) mmol), and the solution was evaporated (45–50°, 15 Torr) to a yellow oil, 0.1-mmol samples of which were sealed into ampoules, heated at 150° for 24 hr, and worked up as above.

Reaction of Tripentylamine with Silver Nitrate.—(a) A solution of 425 mg (2.50 mmol) of $AgNO_3$ and 50 μl (0.171 mmol) of tripentylamine in 3 ml of nitrobenzene was heated at 110° for 24 hr. Metallic silver was deposited as a mirror and a powdery precipitate, which was filtered and washed with ether. The filtrate was made up to 10.0 ml with ether and analyzed by the standard gc procedure. (b) A solution of 124 mg (0.726 mmol) of $AgNO_3$ and 100 μl (0.342 mmol) of tripentylamine in 3 ml of *tert*-butyl alcohol was refluxed for 24 hr and worked up as in (a). (c) A mixture of 117 mg (0.687 mmol) of $AgNO_3$ and 100 μl (0.342 mmol) of tripentylamine was heated at 110° for 24 hr and worked up as in (a).

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—Di-*n*-pentylnitrosamine, 13256-06-9; silver nitrate, 7761-88-8; carbon tetrachloride, 56-23-5; tetrapentylammonium nitrate, 682-02-0; tripentylammonium nitrate, 41507-71-5; tripentylamine, 621-77-2.

Electron Transfer with Aliphatic Substrates. Oxidation of Cyclohexane with Cobalt(III) Ions Alone and in the Presence of Oxygen

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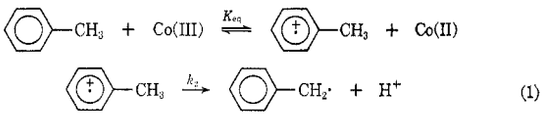
An electron-transfer mechanism is proposed for the oxidation of cyclohexane involving initial interaction of C–H σ bonds with cobalt(III) ions. This mechanism is much broader in scope than the presently accepted radical cation concept limited to alkylbenzenes. In the light of our findings, formation of radical cations with alkylbenzenes is treated as an accompanying phenomenon. In the oxidation of cyclohexane with cobaltic acetate, major products were cyclohexyl acetate, 2-acetoxycyclohexanone, and cyclohexylidene diacetate. Minor products included cyclohexanol, cyclohexanone, and bicyclohexyl. Reactivities of cyclo aliphatic substrates toward cobalt(III) ions investigated followed the sequence *cis*-decalin > *trans*-decalin > *cis*-1,2-dimethylcyclohexane ~ toluene > *trans*-1,2-dimethylcyclohexane > cyclohexane ~ cyclohexane-d_{12} > methylcyclohexane > *trans*-1,4-dimethylcyclohexane, indicating a significant steric effect, just as found with several alkyl aromatics. Oxidation of cyclohexane in the presence of cobaltic acetate and oxygen afforded adipic acid as the major product. Similar reactivities for cyclohexane and also for methylcyclohexane toward cobalt(III) ions alone or with cobalt(III) ions in the presence of oxygen suggest rate-determining electron transfer from the substrate to cobalt(III) ion, both in the presence and absence of oxygen.

A new system for oxidizing alkylbenzenes in the presence of large amounts of cobaltic acetate was described in 1960.[1] Recent papers in this area have dealt mostly with the oxidation of toluene.[2-6] Heiba, *et al.*,[7] in a more recent paper, attempted to finalize the mechanism and suggested the intermediacy of radical cations through isolation of nuclear and side chain substituted products. With several substrates, radical cations were detected by esr spectroscopy.[8] They suggested a mechanism, similar to that proposed by Dewar[9] for the manganic acetate oxidation of *p*-methoxytoluene. This electron-transfer concept offered an explanation for the changed reaction parameters of the new system which required a mechanism different from oxidation by a free radical pathway (eq 1). The rate constant is a product of K_{eq} and k_2, the rate-limiting step.



(1)

In our work, attention has been focused on the aliphatic portion of alkyl aromatic substrates as it is clearly the one undergoing oxidative attack. We compared relative reactivities of primary (methyl), secondary (ethyl), and tertiary (isopropyl) alkyl substituents attached to the aromatic nucleus. In the oxidation of *p*-cymene preferential methyl group oxidation was ob-

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