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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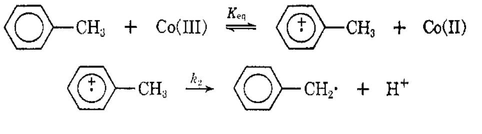
An electron-transfer mechanism is proposed for the oxidation of cyclohexane involving initial interaction of C–H σ bonds with cobalt(III) ions. This mechanism is much broader in scope than the presently accepted radical cation concept limited to alkylbenzenes. In the light of our findings, formation 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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[1] W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

[2] K. Sakota, Y. Kamiya, and N. Ohta, *Can. J. Chem.*, **47**, 387 (1969).

[3] T. A. Cooper and W. A. Waters, *J. Chem. Soc. B*, 687 (1967).

[4] Y. Ichikawa, G. Yamashita, M. Tokashiki, and T. Yamaji, *Ind. Eng. Chem.*, **62**, 38 (1970).

[5] T. Morimoto and Y. Ogata, *J. Chem. Soc. B*, **62**, 1353 (1967).

[6] Y. Kamiya and M. Kashima, *J. Catal.*, **25**, 326 (1972).

[7] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 6830 (1969).

[8] R. M. Dessau, S. Shih, and E. J. Heiba, *J. Amer. Chem. Soc.*, **92**, 412 (1970).

[9] P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966).

served.[10] Methyl group attack was also prevalent in the oxidation of 1,1-di(*p*-tolyl)ethane and 1,1-di(3,4-dimethylphenyl)ethane.[11] Subsequently, purely aliphatic substrates, such as *n*-butane,[12] *n*-pentane,[12] and cyclohexane, were found to react under identical conditions with formation of carboxylic acids in high selectivity. Oxidation of methylcyclohexane and isobutane proceeded at comparatively lower rates, following a pattern shown in the oxidation of branched chain alkyl aromatics. These observations indicate basically the same mechanism operating in both the oxidation of alkane and alkylbenzenes involving electron transfer from C–H σ bond to Co(III) ion. No reason is seen for a different pathway for alkyl aromatic substrates which appropriately should be considered phenyl-substituted alkanes.

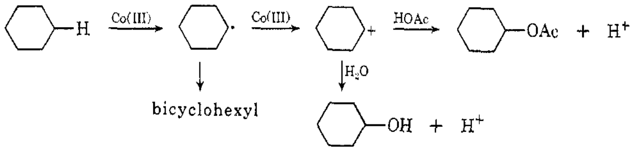
Results and Discussion

Oxidation of Cyclohexane with Cobaltic Acetate.—To elucidate the interaction of cobaltic ion with aliphatic substrates, cyclohexane was treated with cobaltic acetate in acetic acid in the absence of oxygen at 78–80°. The stoichiometry for this reaction was ~7.5 mmol of Co(III)/mmol of cyclohexane reacted at 1.6% hydrocarbon conversion. This ratio is considerably higher than for the oxidation of toluene in the same system, suggesting further oxidation of primary products. The rate of cyclohexane attack by Co(III), however, was slower than for toluene.

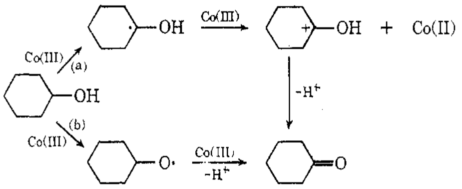
Major products of the reaction were 2-acetoxycyclohexanone (48.8 wt %), cyclohexyl acetate (35.4), and cyclohexylidene diacetate (14.0), identified by vpc by doping with standards and confirmed by mass spectroscopy by their fragmentation patterns. Minor products detected by vpc were cyclohexanone, cyclohexanol, and bicyclohexyl. These products accounted for ~69% of Co(III) ions reduced.

With oxygen excluded from the system, oxygenated derivatives probably arose from interactions involving water of hydration from $Co(OAc)_2 \cdot 4H_2O$[13] or the hydroxyl ligands in $Co(OAc)_5OH$ and $Co(OAc)_4(OH)_2$.[14,15] In agreement with observed stoichiometry, the pathways in Schemes I–III account for the majority of the products. Their nature suggests cyclohexanone as an intermediate, which in turn can be produced from cyclohexanol. Preferential capture of cyclohexyl carbonium ions by the more nucleophilic hydroxyl rather than the acetate ions, explains the observed product distribution. Direct interaction of Co(III) ions with the C–H σ bond is apparent. This is consistent with observations of Waters, *et al.*,[3] who found the oxidation of cyclohexane with Co(III) ions and oxygen to be first order with respect to both cyclohexane and Co(III) in aqueous acetonitrile. Additional evidence is the fact that oxidation of cyclohexane with Co(III) salt in the presence of 0.2 *M* cupric acetate, a common radical terminator *via* electron transfer, proceeded without difficulty. This indicates that the reaction is not dependent on hydrogen abstraction by free radicals. Therefore, C–H σ bonds are the electron donors to the Co(III) ion.

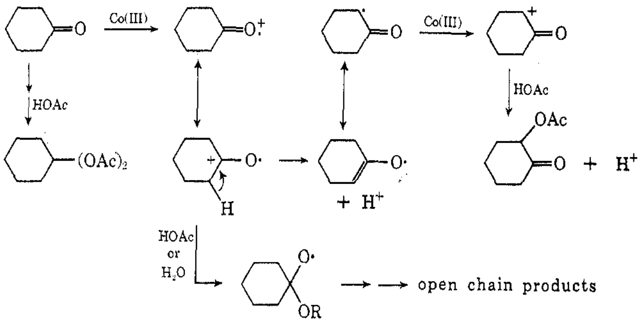
SCHEME I



SCHEME II



SCHEME III



(RO = OH, OAc, etc)

In the presence of oxygen, the mechanism must include interactions between cyclohexyl radicals and oxygen, as well as one or more regenerative steps for Co(II)–Co(III).

Oxidation of Cyclohexane with Co(III) Salt and Oxygen.—Oxidation of cyclohexane with cobaltic acetate and oxygen in acetic acid [95° (1.7 atm)] gave adipic acid as the main product (up to 75% efficiency, 45% conversion) along with smaller amounts of glutaric and succinic acids. Minor products included cyclohexyl acetate, lactones (ir), and unknown materials. Results with cyclohexane (Table I) under conditions identical with those employed in the oxidation of alkyl aromatics with Co(III) ions are surprising. The rate of cyclohexane oxidation again was found to depend on Co(III) ion concentration as in the case of the alkyl aromatic substrates (Table II).

To our knowledge, these experiments are the first examples of alkane oxidation by cobalt acetate. High selectivity and conversion to adipic acid distinguish this reaction from the classical free-radical oxidation of cyclohexane.

Relative Reactivities.—To determine the effect of structure on reactivity, rates of several cycloaliphatic substrates toward Co(III) ions were determined and compared to those observed in typical free-radical reactions (Table III). Relative reactivities for cyclohexane and methylcyclohexane were obtained by competitive oxidation with Co(III) ions alone. Reactivities were also determined for these substrates in the presence of Co(III) ions and oxygen, as well as for several other cycloalkanes. In view of nearly identical reactivities for these substrates in both systems,

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[10] A. Onopchenko, J. G. D. Schulz, and R. Seekircher, *J. Org. Chem.*, **37**, 1414 (1972).

[11] A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, **37**, 2950 (1972).

[12] J. G. D. Schulz and A. Onopchenko, *J. Org. Chem.*, **38**, 909 (1973).

[13] Cobaltic acetate was prepared from $Co(OAc)_2 \cdot 4H_2O$.[7]

[14] S. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 5196 (1968).

[15] A. Tkac, K. Vesely, and L. Omelka, *J. Phys. Chem.*, **75**, 2575 (1971).

TABLE I

OXIDATION OF CYCLOHEXANE[a]

Expt	Reaction time, hr	Cyclohexane reacted, g (%)	Adipic acid, g (% efficiency)	Glutaric acid, g (% efficiency)	Succinic acid, g (% efficiency)	Other products[c]
1	2	35.4 (28.1)	39.1 (63.5)	8.1 (14.6)	2.9 (5.8)	16.0
2	2	32.3 (25.6)	36.1 (64.3)	6.5 (12.8)	2.5 (5.5)	12.2
3	3	45.3 (36.0)	53.9 (68.4)	9.7 (13.6)	3.3 (5.2)	14.0
4	3	44.7 (35.5)	50.4 (64.9)	8.9 (12.7)	3.0 (4.8)	11.0
5	4	55.1 (43.7)	61.6 (64.3)	10.7 (12.3)	3.3 (4.5)	8.5
6	5	56.9 (45.2)	65.4 (66.1)[d]	9.8 (11.0)	3.6 (4.5)	9.2

[a] At 95°, 1.7-atm oxygen pressure. Reactants: 126 g of cyclohexane, 300 g of HOAc, 3.7 g of cyclohexanone,[b] 9.4 g of $Co(OAc)_2 \cdot 4H_2O$. [b] Added as an initial source of peroxy radicals. [c] Weight per cent of total area by vpc. Minor products were cyclohexanone (trace), cyclohexanol (trace), cyclohexyl acetate, lactones (trace), and unknowns. Analysis was by vpc using internal standard procedure. Acids are by isolation. [d] Efficiencies approached 75% in some runs.

TABLE II

EFFECT OF CATALYST CONCENTRATION ON REACTION[a]

Expt	Reaction time, hr	Cyclohexane reacted g (%)	Adipic acid, g (% efficiency)	$Co(OAc)_2 \cdot 4H_2O$, g (wt % of HOAc)	Productivity, g of adipic acid/hr
1	8	66.6 (52.9)	67.1 (57.9)	9.4 (3.1)	8.4
2	8	59.8 (47.5)	59.8 (57.6)	4.7 (1.6)	7.5
3	8	51.7 (41.0)	46.6 (51.9)	3.6 (1.2)	5.8
4	5	26.6 (21.1)	23.1 (50.0)	2.4 (0.8)	4.6

[a] At 75°, 1.7-atm oxygen pressure. Reactants: 126 g of cyclohexane, 300 g of HOAc, 3.7 g of cyclohexanone.

TABLE III

REACTIVITY OF SELECTED HYDROCARBONS TOWARD Co(III) ION AND SOME RADICALS[a]

Hydrocarbon	Registry no.	Co(III), 78°	Co(III) + O_2, 100° (20 atm)	Ph·, 60°,[b] predicted reactivity	t-BuO·, 40°,[b] predicted reactivity
cis-Decalin			2.4 (34.7)[c]		
trans-Decalin			1.4 (10.6)[c]		
cis-1,2-Dimethylcyclohexane	2207-01-4		1.1		
Toluene[d]		1.00	1.00 (1.00)[c]	1.00	1.00
trans-1,2-Dimethylcyclohexane	6876-23-9		0.6		
Cyclohexane	110-82-7	0.50	0.47	3.6	6.0
Cyclohexane-d_{12}	1735-17-7	0.42			
Methylcyclohexane	108-87-2	0.19	0.24	4.6	6.6
Cumene	98-82-8	0.3[e]	0.2	2.9	2.3
trans-1,4-Dimethylcyclohexane	2207-04-7		0.1		
Chlorobenzene or *o*-dichlorobenzene[f]					

[a] Relative reactivities per molecule. [b] Calculated from data of Table VI of W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972). [c] These are reactivities obtained from autoxidation rates. See F. Jaffe, T. R. Steadman, and R. W. McKinney, *ibid.*, **85**, 351 (1963), ref 8, and G. A. Russell, *ibid.*, **78**, 1047 (1956). [d] Assumed standard. [e] Reference 8, 65°. [f] Internal standard.

interaction of the hydrocarbon with Co(III) ions appears to be the rate-limiting step. This phenomenon was earlier observed with aromatic substrates.

Reactivities in the cobalt system are different from those predicted for typical free-radical abstractions by Ph· and *t*-BuO· radicals. This is particularly evident when compounds with tertiary hydrogen atoms such as methylcyclohexane, dimethylcyclohexanes, and cumene are considered. Lack of reactivity of the tertiary hydrogen appears to be associated with steric effects of both catalyst and substrate. The observed reactivity of toluene toward Co(III) ions is about twice that of cyclohexane. Higher rates with toluene, which on a per hydrogen basis is about eight times as reactive as cyclohexane, are due to the activating effect of a phenyl group on the C–H σ bond.

Finally, rates for oxidation of cyclohexane and perdeuteriocyclohexane by cobaltic ions were compared to each other, showing no isotope effect (Table IV). Earlier investigators have used cobalt compounds in catalytic amounts mostly for initiation.[16–19] Our results, however, are consistent with a mechanism in which metal ions act as chain carriers.

Kinetic Isotope Effect. Identical reactivities of cyclohexane toward Co(III) ions in the presence or absence of oxygen and rate dependence on Co(III) ion concentration suggest initial interaction of metal ions with the substrate. The nature of this interaction is not clear. It was of interest, therefore, to compare the oxidation rate of cyclohexane with that of the deuterated substrate and to observe a possible kinetic isotope effect. Because of the multiplicity of products formed in our system, even at low conversion level and high dilution, reactivities had to be based on the disappearance of the substrates, cyclohexane and cyclo-

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(16) P. W. Sherwood, *Petrol. Process.*, **11** (5), 74 (1956).

(17) M. Sittig, *Hydrocarbon Process. Petrol. Refiner*, **41** (6), 181 (1962).

(18) I. V. Berezin, E. T. Denisov, and N. M. Emanuel, "The Oxidation of Cyclohexane," Pergamon Press, New York, N. Y., 1966.

(19) N. M. Emanuel, Ed., "The Oxidation of Hydrocarbons in the Liquid Phase," Pergamon Press, New York, N. Y., 1965.

TABLE IV

COMPETITIVE OXIDATIONS OF C_6H_{12}–C_6D_{12} MIXTURES WITH Co(III) IONS[a]

Expt	Temp range, °C	k_H/k_D[b]
1	78–80	0.85[c]
2	70–72	0.95[d] (0.86)[e]
3	40–42	0.80[f]
	Av	0.86

[a] *Ca.* 0.22 *M* Co(III) in HOAc and 0.1 *M* in C_6H_{12}, C_6H_{12}, and either in C_6H_6 or C_6H_5Cl as internal standard; experiments were 13–16 hr in duration in an inert atmosphere. [b] Analyses were carried out by mass spectrometry. Relative reactivities were calculated from

$$k_H/k_D = \log([I_A/I_S]_f/[I_A/I_S]_i)/\log([I_B/I_S]_f/[I_B/I_S]_i)$$

where I = intensity, A = C_6H_{12}, B = C_6D_{12}, and S = internal standard. Subscripts refer to initial and final molar concentrations. [c] In the presence of 1.0 *M* $NaOAc \cdot 3H_2O$. [d] In the presence of 0.3 M $NaOAc \cdot 3H_2O$. [e] Analysis of *n*-C_5 extract. [f] In the presence of 1.2 M LiCl to increase reactivity of Co(III), at the lower temperature.

hexane-d_{12}, a technique earlier used to determine the isotope effect in toluene oxidation.[7]

Reactivities of cyclohexane *vs.* cyclohexane-d_{12} (k_H/k_D) ranged from ~0.80 to 0.95 (average 0.86) in the range of 40–80°. The small inverse deviation of the k_H/k_D ratio from unity is considered to be within the limits of experimental error, although even small values could be explained on the basis of inductive and polarization differences of the C–D bond.[20] With aliphatic substrates, therefore, loss of proton does not occur in the rate-controlling step. In several of our experiments, rates increased with the addition of Co(III) ions and decreased with the addition of Co(II) ions, indicative of an equilibrium situation. Results are consistent with a two-step mechanism (eq 2) where

$$\begin{gathered} RH + Co(III) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^+ + Co(II) \\ X^+ \xrightarrow{k_2} R\cdot + H^+ \end{gathered} \tag{2}$$

X is an electron-deficient species derived from the substrate by loss of an electron. Assuming a steady-state concentration of X^+, $d[X^+]/dt = 0$, the observed rate constant is given by $k_{obsd} = k_1k_2/k_{-1} + k_2$. When k_2 is small, *i.e.*, $k_2 \ll k_{-1}$, this expression can be approximated by $k_{obsd} = K_{eq}k_2$, as observed with aromatic substrates.[7] When k_2 is large, *i.e.*, $k_2 \gg k_{-1}$, the expression simplifies to $k_{obsd} = k_1$. The kinetic isotope ratio would then be represented by $k_H/k_D = k_{1H}/k_{1D}$. Since breaking or formation of C–H bonds is not involved in the proposed mechanism, the k_H/k_D ratio is expected to be close to unity. Also consistent with this scheme is the observation of an approximately constant k_H/k_D ratio over a wide temperature interval.

We therefore favor a mechanism in which the reaction proceeds over an equilibrium step, in which breaking or formation of C–H bonds is not rate controlling.

Mechanism.—We found that paraffins are oxidized by cobaltic ions and oxygen to carboxylic acids with high selectivity under conditions critical for alkylbenzene oxidation. Oxidations of paraffins and alkylbenzenes in this system appear analogous in the following respects: (1) high rates are observed at low temperature, (2) reactions are limited to Co(III) as the effective oxidant, (3) high selectivities to carboxylic acids are observed, (4) tertiary hydrogen is unreactive, often decreasing the reactivity of the substrate, (5) rates are dependent on Co(III) ion concentration, and (6) reactions are not inhibited by cupric ions. These observations suggest a similar mechanism for alkanes and alkylbenzenes. The π system therefore need not be invoked as a prerequisite for electron transfer to Co(III) ions. Interaction of the C–H σ bonds with Co(III) ions should satisfy oxidation of both hydrocarbon types.

The oxidation of alkanes and alkylbenzenes in this system differ in one respect. A kinetic isotope effect is observed with aromatic substrates (k_H/k_D, 3.7),[7] but not with the alkanes. This can be reconciled with a mechanism in which the rate-controlling step is governed by K_{eq} or k_2, depending on the stability of RH^+ (eq 3). For aromatic substrates K_{eq} is large compared to K_{eq} for the alkanes, where it is rate determining. Stabilization of RH^+ can occur to a varying degree through solvation, or redistribution of charge over several atoms *via* induction, resonance, or hyperconjugation. With initial attack at the σ C–H bond, the proposed mechanism is much broader in scope and not limited to alkylbenzenes, but applicable to other hydrocarbon substrates, including the alkanes. An accompanying phenomenon, formation of nuclearly substituted products in the the reaction of alkylbenzenes with Co(III) salts and added nucleophiles, could be rationalized assuming appropriate resonance structures which, however, need not be invoked for σ electron transfer.

$$\begin{gathered} RH + Co(III) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RH^+ + Co(II) \\ RH^+ \xrightarrow{k_2} R\cdot + H^+ \end{gathered} \tag{3}$$

Elucidation of the structure of the active cobalt species and the effect of changed ligands and added nucleophiles, or of the nature of the solvent system, are beyond the scope of this paper.

Experimental Section

Oxidation of Cyclohexane with Cobalt(III) Acetate and Oxygen.—Oxidations were carried out in a 1-l., 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie, Pa.). A typical procedure used for the oxidation of cyclohexane is described in detail for an experiment at 104° and 20 atm of total pressure. A mixture consisting of 20 g of $Co(OAc)_2 \cdot 4H_2O$, 15 g of MEK, and 60 g of cyclohexane in 400 g of glacial acetic acid was charged into the autoclave. The autoclave was brought to the operating temperature and pressure, and held there for 3 hr. The autoclave was cooled and depressured, and the product mixture was removed. The crude product mixture, 545.0 g, was analyzed for water (5.7%), MEK (0.6%), and cyclohexane (0.5%) by vpc using acetone as internal standard. The low boiling components and solvent were removed under reduced pressure in a rotary evaporator, the residue was boiled in 300 ml of water until the solution had turned from dark green to pink, and the mixture was evaporated to dryness. The product was separated from the catalyst by extraction with acetone. Analysis of the isolated product showed 51.8 g (52.0% selectivity) of adipic acid, 7.8 g (8.6) of glutaric acid, and 17.8 g (22.2) of succinic acid to be in a mixture. Conversion of cyclohexane was ~95%. Analyses of experiments in Tables I and II were done by vpc employing 20% Carbowax 20M column and internal standard procedure.

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[20] Lars Melander, "Isotope Effects on Reaction Rates," The Ronald Press, New York, N. Y., 1960.

Oxidation of Cyclohexane with Cobalt(III) Acetate.—A total of 23.7 g (285 mmol) of cyclohexane and 130 ml of 0.27 *M* cobalt(III) acetate in acetic acid were stirred under nitrogen atmosphere for 3 days at 70° until Co(III) ions were consumed. The mixture was cooled, diluted with water, saturated with NaCl, and extracted with ethyl ether. The organic layer was washed with water, dried with $MgSO_4$, and concentrated in a rotary evaporator to a volume of ~2 ml. Analysis by vpc identified the following products in order of their appearance on the chromatogram (10 ft × 0.25 in., 10% Carbowax 20M column at 90°): bicyclohexyl (1.8 wt %), cyclohexanone (trace), cyclohexyl acetate (35.4), cyclohexanol (trace), cyclohexylidene diacetate (14.0), and 2-acetoxycyclohexanone (48.8). On the basis of stoichiometry, 4 mol of Co(III) required/mol of cyclohexylidene diacetate, 2 mol/mol of cyclohexyl acetate, and 6 mol/mol of 2-acetoxycyclohexanone, the products accounted for ~69% of the oxidant consumed. The aqueous layer also contained small quantities of cyclohexanone and cyclohexanol which were not determined as well as open-chain products of cyclohexane on the basis of nmr, but their structures have not been established with certainty. Conversion of cyclohexane was ~1.6%. Major products were also identified by their fragmentation patterns (vpc–mass spectrum).

Competitive Rate Study.—Competitive oxidations on mixtures of substrates were done under conditions earlier described.[10] Initial concentration of each substrate was held at a low value (~1.0 *M*) to minimize possible solvent effects. After the initiation period was over, reaction was allowed to proceed for 5 min. Initial charge and the pentane extract of the final mixture were analyzed directly by vpc for the disappearance of starting hydrocarbons. Analyses were carried out by vpc using 20 ft × 1/8 in., 20% Carbowax 20M column (Hewlett-Packard 7620A research chromatograph, TC detector), and chlorobenzene or *o*-dichlorobenzene as internal standard. Peak areas were electronically measured. All reactivities were related to toluene using eq 4

$$\frac{k_a}{k_b} = \frac{\log([A]_f/[A]_i)}{\log([B]_f/[B]_i)} \qquad (4)$$

where [A] and [B] refer to concentrations of the two substrates before and after the reaction in weight per cent.

Competitive oxidations with cobaltic salts alone were carried out in sealed ampoules under nitrogen atmosphere.

Acknowledgments.—The authors wish to thank Mr. H. T. Best and Mr. J. T. Swansiger for their work on mass spectral analyses.

Registry No.—Cobalt(III) ion, 7440-48-4; cobalt(III) acetate, 917-69-1.

Cleavage of Saturated Fatty Acid Amides by Anhydrous Hydrogen Fluoride–Boron Trifluoride

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N-n-Butylamides of long-chain, unbranched carboxylic acids undergo degradation, isomerization, and (in part) dimerization of the fragments when treated at 0–5° with liquid hydrogen fluoride saturated with boron trifluoride. The compounds studied were the *N-n*-butylamides of undecanoic, myristic, palmitic, and stearic acid. Two major classes of products were obtained: (1) saturated, branched *N-n*-butylamides and (2) saturated, branched *N,N'*-di-*n*-butyldiamides. The ratio of the former to the latter is 2:1. The products from *N-n*-butylundecanamide consist mainly of the following *N-n*-butylamides (relative proportions): 5-methylhexanamide (12.9%), 6-methylheptanamide (25.6%), 5-methylheptanamide (18.5%), 7-methyloctanamide (14.5%), and 6-methyloctanamide (6.5%). The branched diamides are predominantly of chain length C_{12}–C_{15} (acid moiety). Similar results are obtained with *N-n*-butylmyristamide, *N-n*-butylpalmitamide, and *N-n*-butylstearamide when treated under the indicated reaction conditions; however, *N-n*-butylamides of acid moiety chain length shorter than C_{10} (*e.g.*, the *N*-alkyloctanamide) are not affected. The probable mechanism of the reaction is discussed, and it is concluded that the inductive effect of the protonated amide group is important in determining the product distribution.

Acid-catalyzed isomerization and degradation reactions of saturated hydrocarbons have been extensively studied because of their practical importance in the petroleum industry.[2] This work has led to an understanding of certain fundamental aspects of these reactions and has also revealed interesting transformations such as the isomerization of *endo*-trimethylenenorbornane to adamantane.[3] Recently, new reactions in superacid media, such as direct alkylation and nitration of alkanes, have been explained as occurring by the intervention of pentacoordinated carbonium ions,[4,5] a development that has spurred additional interest in this field. However, there have been only scattered studies on the transformations of fatty acid derivatives under strongly acidic conditions.[6–9] The investigation of these reactions is rendered more complex by the presence of the carbonyl group; important questions about the effect of the functional group on the reactivity of C–C and C–H bonds in other parts of the molecule need to be answered. We report here the cleavage reactions of secondary aliphatic amides in the acidic medium hydrofluoric acid–boron trifluoride (HF–BF_3).

Results

In a typical experiment, one of the *N-n*-butylamides **1a–1g** (0.006 mol) was dissolved in 12 ml of liquid HF at 0–5° followed by saturation of the solution with

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