bromide. The liquid was carefully fractionated at reduced pressure. A fraction, bp 70–100° (18 Torr), 2 g, containing the major peaks of this discharge reaction was further separated by preparative gas chromatography. Some of the peaks were identified as follows.

Perfluoro-1,4-dibromobutane (0.7%) was identified as above.

Fluorotribromomethane[9] (0.5%) had ^{19}F nmr CF ϕ −7.5.

1,1,2-Trifluoro-1,2,2-tribromoethane[11-13] (6%) had ^{19}F nmr CF_2Br ϕ 58.7 (d, J = 17.9 Hz), $CFBr_2$ 69.6 (t); ir 8.42 (s), 8.65 (m), 9.05 (m), 9.15 (s), 9.95, 10.05 (s), 12.0 (s), 13.85 (s), 14.6 μ.

Three other peaks (area ratios 0.8, 0.4, and 1.5%) were unsaturated as shown by ^{19}F nmr (ϕ 56.8 and 59.7) and ir (5.85 and 5.89 μ). These structures were complicated. Other small peaks (total 6.1%) were not identified.

Registry No.—TFE, 116-14-3; Br_2, 7726-95-6; fluorotribromomethane, 353-54-8; 1,1,2-trifluoro-1,2,2-tribromoethane, 354-49-4.

Acknowledgments.—The authors are indebted to Mr. E. Kutch for running the electrical discharge reactions and to J. Christakos for the mass spectral determinations.

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Oxidation of *n*-Butane with Cobalt Salts and Oxygen *via* Electron Transfer

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Low-temperature Co(III) ion promoted oxidation of *n*-butane affords acetic acid selectively. Yields of the C_2 acid around 84%, assuming 2 mol of acid/mol of butane, require predominant cleavage of the 2–3 bond. In view of the dependence of rate on Co(III) ion concentration, the ineffectiveness of Mn(III) ions in this reaction, and other general characteristics which were also observed with alkylbenzenes, results are rationalized in terms of an electron transfer pathway in which cobalt ions function as chain carriers.

A new system for reacting alkylbenzenes with oxygen in the presence of large concentrations of cobaltic acetate was reported in 1960.[1] Later papers in this area dealt mostly with toluene oxidations.[2-5] To account for the vastly different parameters of this system compared to those of conventional free radical processes, an electron transfer concept was advanced.[6,7] While oxidation of alkylbenzenes *via* electron transfer was thought to depend on the presence of a π system,[6,7] satisfactory evidence to justify this postulate was not presented. Since side chains are the entities undergoing chemical change in alkylbenzene oxidations, it was of interest to investigate oxidation of purely aliphatic substrate in this system. With *n*-butane as the model, oxidation of this purely aliphatic substrate was found to depend on the same parameters that are critical in the oxidation of alkylbenzenes. Butane oxidation is an example of electron transfer from C–H σ bond to Co(III) ion. Electron transfer, therefore, is a general phenomenon operating on C–H σ bonds and not limited to π systems.

Results

Products of the low-temperature Co(III) ion promoted oxidation of *n*-butane are acetic acid (83.5% yield, average of three experiments, Table I), propionic acid (5.4%), *n*-butyric acid (3.5%), and methyl ethyl ketone (MEK)(4.4%). Butane conversions were around 78%. Minor products (<2%) include varying amounts of methyl and ethyl formates, methyl, ethyl, and propyl acetates, traces of acetaldehyde as well as biacetyl, but no formaldehyde or formic acid. Identical results were obtained in both flow and closed systems. Experimental conditions, products obtained, and other data are summarized in Table I. In the oxidation of butane a considerable amount of water is formed during the first few minutes, much more than could be accounted for by the liquid products formed. We have attributed this to total combustion of MEK during initiation. To test this assumption, small amounts of water, known to inhibit MEK oxidation, were added. It was found that, with *ca.* 4.5% of water in the charge, combustion of MEK to CO_2 and H_2O was virtually eliminated. With 9% of water in the acetic acid phase, oxygen absorption diminished substantially. To determine what proportion of MEK was initially converted into CO_2 and H_2O, a control experiment was carried out with MEK alone in the concentration employed for initiation. Of the MEK charged, about 45% was consumed by total combustion. Calculations in Table I were made on a loss free basis assuming that MEK found in the reaction mixture was produced from butane, and that only 55% of MEK added for promotion was converted into acetic acid. At a pressure of 20 atm, highest rates and best acetic acid yields were obtained at temperatures ranging from 100 to 125°. At 80°, oxidation was very slow. Above 130°, rates decreased due to a lower partial pressure of oxygen in the system.

Oxidation of *n*-pentane (104°, 17 atm, 4 hr, ~45% conversion) gave acetic acid and propionic acid in yields of 48 and 27%, respectively. *n*-Butyric acid, *n*-valeric acid, and 2- and 3-pentanones were also formed in smaller amounts. Formic acid was not observed under our conditions.

Oxidation of isobutane (80 g) under conditions of expt 3 afforded 2.5 g of acetone, 6.6 g of *tert*-butyl alcohol, and 3.1 g of methanol (~10% conversion). The lower reactivity of isobutane compared to the *n*-butane is attributed to steric hindrance with the

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TABLE I

OXIDATION OF n-BUTANE[a]

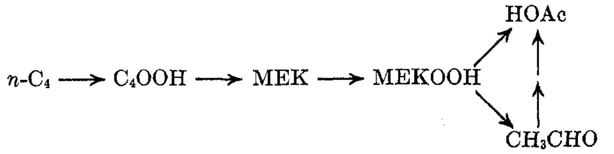
	Expt no.			
	1^{b}	2^{c}	3^{c}	4^{i}
Charge data, g				
n-C_4H_{10}	185	157	157	70
HOAc	345	280	280	100
$Co(OAc)_2 \cdot 4H_2O$	25	20	20	0.12
MEK[d]	28	20	20	
Conditions				
Pressure, atm[e]	17	21.6	24	20[j] (155°)
Reaction time, hr	4	4	2	3.5
Products, g (% selectivity)				
HOAc[f]	245.7 (83.3)	207.0 (82.8)	220.0 (84.6)	106.8 (41.0)[k]
C_3 acid	8.9 (4.9)	9.1 (5.9)	8.5 (5.3)	2.0 (1.2)
C_4 acid	4.3 (2.0)	7.3 (4.0)	8.5 (4.4)	
MEK[g]	5.5 (3.1)	7.3 (4.9)	8.5 (5.4)	18.8 (12.0)
Misc oxygend products[h]	4.4	2.1	2.0	120.8 (45.8)[l]
Water	59.0	48.2	51.1	
Total	327.8	281.0	298.6	248.4
Conversion data				
C_4 conversion g (%)	142.5 (77)	120.9 (77)	125.6 (80)	125.6 (24)
C_4 lost on venting	16.6 (9)	13.6 (8.7)	5.0 (3.2)	
C_4 recovered	25.9 (14)	22.5 (14.3)	26.4 (16.8)	
Efficiency to total acids, %	90.2	92.7	94.3	~42

[a] 110°. [b] Flow system; exit gases withdrawn at *ca.* 1 l./hr. [c] Closed system. [d] Assumed all reacted during initiation period: *ca.* 55% going to HOAc, and *ca.* 45% to carbon dioxide and water; yield of HOAc was corrected accordingly. [e] Total pressure (mostly partial pressures of C_4 and oxygen). [f] Acid formed from C_4, assuming 2 mol of HOAc/mol of C_4. [g] Formed from butane. [h] Includes varying amounts of methyl and ethyl formates, methyl, ethyl, and propyl acetates, and traces of acetaldehyde, biacetyl, and acetone. Acetone is thought to come mostly from isobutane impurity in the feed. [i] Experiment taken from Table III, 4th run, of ref 16 for comparison purposes. [j] Partial pressure of oxygen. [k] Products are corrected to correspond to 125.6 g of C_4 reacted as in expt 3. [l] Distribution of oxygenated products by wt % was as follows: ethyl acetate (41.5), methyl acetate (18.8), methanol (1.6), 1-butanol (1.1), n-butyl acetate (1.3), acetone (6.5), ethanol (2.4), carbon dioxide (26.4), and formic acid (2.4).

bulky liganded metal ion. Whatever reaction occurred under conditions employed probably proceeded *via* the normal free radical pathway which is therefore not a significant contributor in the cobalt system. In a competitive oxidation n-butane was at least three times as reactive as isobutane.

Discussion

Low-temperature oxidation of n-butane with large concentrations of cobaltic ion distinguishes itself by its high selectivity (>83%). Radicals are generated by electron transfer from substrate to metal ion with high rates at 100°. Temperatures up to 170°[8] and higher, on the other hand, are required for thermal formation of radicals in classical free radical processes which employ small amounts of metal salt solely for initiation.[9-11] Noncatalytic butane oxidation of this latter type affords acetic acid in about 40% efficiency as only one component in a complex mixture of oxygenated species. The preceding general pathway has been proposed.[11-14]



$$\begin{tikzcd} & & & & HOAc \\ n\text{-}C_4 \arrow[r] & C_4OOH \arrow[r] & MEK \arrow[r] & MEKOOH \arrow[ur] \arrow[dr] & \\ & & & & CH_3CHO \arrow[uu] \end{tikzcd}$$

These reactions could also occur under electron transfer conditions, but should be negligible at low temperatures. For electron transfer the sequence n-$C_4 \rightarrow$ MEK $\rightarrow Ac_2 \rightarrow$ 2HOAc is favored in which butane reacts with Co(III) in the initiation step. Propagation again involves oxidation of butane by Co(III), as well as reduction of C_4 and MEK peroxy radicals by Co(II). While a thorough study has not been completed, the presence of biacetyl (Ac_2) in all reaction mixtures allows some speculation as to the mechanism involved. Biacetyl was found to be more reactive than MEK under the oxidation conditions, producing acetic acid in high selectivity. Formation of the symmetrical intermediate is consistent with high selectivity to acetic acid, requiring predominant cleavage of the 2–3 butane bond.

Conversion of Co(II) into Co(III) precedes the maximum oxidation rate. Shortening and final elimination of induction periods with increasing Co(III) ion concentration is further evidence for the interaction of substrate with cobaltic ion. This rate dependence is shown in Table II. Requirements for large amounts of metal salt is in contrast to commercial butane oxidations which are dependent on direct oxygen trans-

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(8) The patent literature alone dealing with the liquid phase oxidation of C_3–C_6 paraffins runs into hundreds of patents; therefore, no attempt was made to provide a comprehensive review.

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TABLE II

EFFECT OF CATALYST CONCENTRATION ON BUTANE CONVERSION[a]

$Co(OAc) \cdot 4H_2O$, mol	Butane, mol	HOAc/Butane (molar ratio)	Butane/ $Co(OAc)_2 \cdot 4H_2O$ (molar ratio)	Log (butane/ $Co(OAc)_2 \cdot 4H_2O$)	Butane conversion, %[b]
0.00120	2.90	1.74	2417	3.382	~6.7 (1.0)[d]
0.00683	3.22	1.78	471	2.672	31.5 (4.7)
0.02010	3.07	1.88	153	2.184	40.8 (6.1)
0.100[c,e,g]	3.19	1.81	32	1.505[f]	74.0 (11.1)

[a] 100°, 17 atm, 3 hr. [b] Based on products. [c] Corresponds to *ca.* maximum solubility (~0.3 *M*) in HOAc at room temperature. [d] Estimate of relative rate. [e] Final concentration was 35 mol % Co(III) and 65 mol % Co(II). [f] Plot against conversion gives a straight line. [g] Induction times in this system varied between 15 and 45 min; induction times increased with a decrease in catalyst concentration.

TABLE III

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

Hydrocarbon	Registry no.	Co(III), 78°	Co(III) + O_2, 100°, 20 atm	t-BuO·,[b] 40°	Ph·,[b] 60°	RO_2·,[d] 100°
Toluene	108-88-3	1.00[c]	1.00	1.00	1.00	
Cyclohexane	110-82-7	0.5	0.5	6.0	3.6	
Methylcyclohexane	108-87-2	0.2	0.2	6.6	4.6	
Cumene	98-82-8	0.3	0.2	2.3	2.9	
n-Butane	106-97-8		($\geqslant$3)[e]	1.8	1.6	1
Isobutane	75-28-5		(1)	1.8	1.9	4

[a] Relative reactivities per molecule; chlorobenzene used as internal standard. [b] Predicted reactivities; calculated from data of Table IV of W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, 94, 1632 (1972). [c] Assumed standard, reactivity = 1.00. [d] t-BuO_2·, or *sec*-BuO_2·, ref 13. [e] Not related to toluene.

fer to the substrate,[15] and not on the intermediacy of metal ions. The function of small amounts of metal salt in this case is to decompose hydroperoxides into radicals. No rate changes were observed varying cobalt concentrations at 155°.[16] Rate dependence on metal salt concentration has also been observed in the Teijin TPA process, also proceeding by electron transfer.[17] Facile oxidation of cyclohexane with cobaltic salts and added cupric acetate in the absence of oxygen is additional evidence that the new system is not dependent on hydrogen abstraction by free radicals as cupric ion are effective free radical terminators.[18,19]

Unlike high-temperature (155°)[16] butane oxidation, which prefers manganese catalysts to those of cobalt, low-temperature oxidation of butane by electron transfer has so far been limited to cobalt salts as the effective oxidants. This is attributed to the lower oxidation potential of the Mn(III)–Mn(II) couple compared to that of Co(III)–Co(II) (1.51 *vs.* 1.82 eV).[20] It implies that Mn(III) ions are not sufficiently strong oxidants to abstract electrons from C–H σ bonds. Electron transfer with Mn(III) was successful only with substrates having ionization potentials below 8.0 eV, which excludes simple paraffins and alkylbenzenes.[21] Free radical reactions with manganese salts, *via* $Mn(OAc)_3 \rightarrow \cdot CH_2COOH + Mn(OAc)_2$, occur at higher temperatures.[21]

An interesting phenomenon was found in both the oxidation of paraffins and alkylbenzenes in the cobalt system. Surprisingly, substrates with tertiary hydrogen showed poor reactivity. Isobutane was less reactive than *n*-butane, methylcyclohexane less reactive than cyclohexane, just as cumene was much less reactive than toluene. In a series of normal paraffins, *n*-butane was found to react faster than *n*-pentane, while *n*-undecane was unreactive. This is inconsistent with a normal free radical pathway which predicts increasing reactivity with increasing number of methylene groups in the substrate.[22,23]

Oxidation of paraffins and alkylbenzenes are analogous in the following respects: (1) good rates of oxidation are observed at low temperature, (2) oxidations show unusual selectivity, (3) reactions are limited to Co(III) as the effective oxidants, (4) rates are dependent on Co(III) ion concentration, (5) reactions are not inhibited by cupric ions, and (6) substrates with tertiary hydrogen atoms are the least reactive (Table III). Electron transfer, clearly in evidence, is therefore not limited to π systems. It represents a more general phenomenon operating on C–H σ bonds, the common feature in both hydrocarbon types. In support of this postulate, oxidations of toluene and cyclohexane by cobaltic ions were found to proceed at comparable rates in aqueous methyl cyanide. Reactions were first order with respect to both substrates and Co(III) ions.[4]

The interaction of Co(III) with aliphatic substrates is now under investigation with a number of cycloaliphatic substrates. This work may provide a new avenue towards selective hydrocarbon oxidation.

Experimental Section

Experiments were carried out in a 1-l., 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie,

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Pa.), equipped with a Dispersomax stirrer, a heating mantle, and cooling coils. Instruments for measuring oxygen absorption and formation of carbon dioxide and carbon monoxide were employed to monitor the reaction. Molecular oxygen was used as the oxidant, introduced into the autoclave through a medium porosity, 2-in. o.d. stainless steel sparger. In the closed system, oxygen was supplied at the rate at which it was consumed. In the continuous system, exit gases were removed at about 1 l./hr.

In a typical experiment (expt 3, Table I), 157 g of *n*-butane was charged into the autoclave together with a solution of 20 g of cobaltous acetate tetrahydrate in 280 g of glacial acetic acid as well as 20 g of MEK. This mixture was agitated for 2 hr at 110° and 24 atm of total pressure. The autoclave was then cooled and depressured through a series of Dry Ice–acetone traps, and the product was withdrawn. A total of 615.7 g of material was recovered from the autoclave and an additional 20.3 g of butane from the traps. Analysis was carried out employing standard procedures such as vpc, titration, and distillation. Water of reaction and nonacidic oxygenated products were determined by vpc on a 4-ft Porapak Q column, programmed from 75 to 250° at 10°/min using acetone as the internal standard. Propionic and *n*-butyric acids were chromatographed on a 10-ft 20% sebacic acid column at 135° using isobutyric acid as internal standard. Total acidity was obtained by titration, obtaining the yield of acetic acid by difference. Results were verified by actual isolation of products by distillation. Approximately 5 g of butane was unaccounted for and was assumed to be lost during the venting operation.

Registry No.—Co(III), 22541-63-5; acetic acid, 64-19-7.

Selective Reductions. XVIII. The Fast Reaction of Primary, Secondary, and Tertiary Amides with Diborane. A Simple, Convenient Procedure for the Conversion of Amides to the Corresponding Amines

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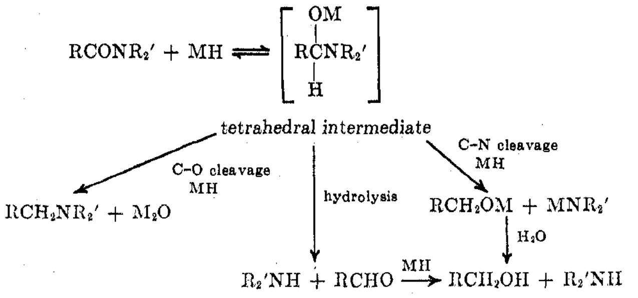
Primary, secondary, and tertiary amide derivatives of both aliphatic and aromatic carboxylic acids were reduced rapidly and quantitatively into the corresponding amines by excess diborane in refluxing tetrahydrofuran. Highly reactive tertiary amides, such as *N,N*-dimethylpivalamide, were reduced at moderate rates even at room temperature. The ease of reduction of the different amide functions, as revealed by the rate studies, follows the order tertiary amide ≥ secondary amide ≫ primary amide. Primary aliphatic amides are reduced at faster rates than primary aromatic amides. Unlike lithium aluminum hydride reductions, the tendency for C–N bond cleavage to yield alcohol is completely absent. The mildness of the reagent, diborane, permits the presence of other substituents less susceptible to the reducing action of the reagent, such as nitro, ester groups, halogen, etc. This reaction provides a convenient synthetic procedure for the selective reduction of amides where this is required in synthetic operations.

Reduction of carboxylic acid amides to the corresponding amines has been examined with a variety of complex metal hydrides and metal hydrides such as lithium aluminum hydride, lithium trimethoxyaluminohydride, aluminum hydride, etc.[2] The most common reagent, lithium aluminum hydride, has been widely applied to such reductions. However, it is very well known that the reaction of lithium aluminum hydride with primary amides is extraordinarily slow and incomplete,[2c] whereas with hindered tertiary amides the yield of the corresponding amine is always quite low owing to side reactions. The tetrahedral intermediate formed initially (Scheme I) undergoes both carbon-oxygen bond rupture leading to the amine, and carbon-nitrogen bond rupture leading to the alcohol. The relative importance of these two pathways depend on (a) steric and electronic characteristics of the amide structure, (b) nature of the reducing agent. Finally, lithium aluminum hydride, lithium trimethoxyaluminohydride, and, to a certain extent, aluminum hydride are exceedingly powerful reducing agents, capable of reducing almost all of the functional groups in an organic molecule. Consequently, this introduces severe limitation in the utility of these reagents for the selective reduction of amides to amines in the presence of other reducible functional groups in a multifunctional substrate.

SCHEME I



We recently reported an extensive investigation of the approximate rates and stoichiometry of the reaction of diborane with organic compounds containing representative functional groups in tetrahydrofuran at 0°.[3] During the course of that investigation, it was observed that primary, secondary, and especially tertiary amides (both aliphatic and aromatic) are reduced by diborane to the corresponding amines rapidly and quantitatively under relatively mild conditions[4] (eq 1).

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[2] (a) For a summary of the literature, see N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, pp 544–592. (b) For a recent review, see J. Zabicky, "The Chemistry of Amides," Interscience, New York, N. Y., 1970, pp 795–801. (c) H. C. Brown, P. M. Weissman, and N. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1458 (1966); H. Uffer and E. Schlitter, *Helv. Chim. Acta*, **31**, 1397 (1948); V. M. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953). (d) H. C. Brown and P. M. Weissman, *J. Amer. Chem. Soc.*, **87**, 5614 (1965). (e) H. C. Brown and N. M. Yoon, *ibid.*, **88**, 1464 (1966). (f) N. M. Yoon and H. C. Brown, *ibid.*, **90**, 2927 (1968).

[3] H. C. Brown, P. Heim, and N. M. Yoon, *ibid.*, **92**, 1637 (1970).

[4] For a preliminary communication on this reaction, see H. C. Brown and P. Heim, *ibid.*, **86**, 3566 (1964).