The Electrical Discharge Reactions of $CF_2{=}CF_2/Br_2$, $CF_2{=}CF_2/BrCF_2CF_2Br$, and $BrCF_2CF_2Br$

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The electrical discharge reactions of $CF_2{=}CF_2/Br_2$, $CF_2{=}CF_2/BrCF_2CF_2Br$, and $BrCF_2CF_2Br$ were studied. In the $CF_2{=}CF_2/Br_2$ system, the major products (63%) were identified as perfluoro-α,ω-dibromoalkanes. Minor amounts of perfluoroalkanes, 1-bromoperfluoroalkanes, and an essentially linear bromine-containing polymeric material were also present. From the $CF_2{=}CF_2/BrCF_2CF_2Br$ system, similar products were obtained; however, a greater proportion of monobromides and polymeric material was formed. A radical mechanism was suggested for these two systems, in which $CF_2{=}CF_2$, $:CF_2$, $\cdot Br$, and $\cdot F$ were considered active species. The electrical discharge reaction of $BrCF_2CF_2Br$ was slow and gave only small yields of $CFBr_3$, $BrCF_2CFBr_2$, $Br(CF_2)_4Br$, and a complicated olefinic mixture.

It has previously been reported[2-7] that electrical discharge reactions of fluoro olefins could be utilized to produce a variety of saturated and unsaturated fluorocarbons. The product mixtures obtained with this process were complex and the mechanisms involved in these reactions were not clear. It was thought that the introduction of another halogen to such systems would minimize the olefinic products and consequently simplify the identification of the discharge products. The present investigation describes the electrical discharge reactions of the following systems: $CF_2{=}CF_2/Br_2$, $CF_2{=}CF_2/BrCF_2CF_2Br$, and $BrCF_2CF_2Br$.

Results and Discussion

The electrical discharge reactions of $CF_2{=}CF_2/Br_2$ and $CF_2{=}CF_2/BrCF_2CF_2Br$ gave good yields of liquid bromofluorocarbons. ^{19}F nmr analysis indicated that both discharge products were essentially linear. Infrared analysis showed the presence of terminal and internal olefinic structures. The amount of unsaturation, however, was less than that present in the tetrafluoroethylene (TFE)[8] or hexafluoropropene[2] discharge products. Gas chromatography indicated that there were significant differences between the distribution of monobromides and dibromides in the two systems.

In the TFE/Br_2 system, the higher bromine concentration favored formation of dibromides (see Table I). It also suppressed the "polymerization" of TFE, as shown by the lesser amount of nonvolatile residue present in this system. The formation of $Br(CF_2)_nBr$, where n = 1–8, indicated that TFE was not only a monomer but also a source of difluorocarbene ($:CF_2$). The presence of monobromoalkanes substantiated the evidence of free fluorine in this discharge. The major reactions in the system can be represented by the following equations.

In the TFE/$BrCF_2CF_2Br$ system, the discharge product contained more of the monobromides and the polymeric fraction (see Table I). $BrCF_2CF_2Br$ reacted more like a telogen than a monomer (see below).

TABLE I
MAJOR COMPONENTS IDENTIFIED FROM THE ELECTRICAL DISCHARGE PRODUCTS OF TFE/Br_2 AND TFE/$BrCF_2CF_2Br$

Structure	Registry no.	TFE/Br_2, %[a]	TFE/ $BrCF_2CF_2Br$, %[a]
C_6F_{14}	355-42-0	1.43	4.53
n-C_4F_9Br	375-48-4	2.56	6.91
n-$C_5F_{11}Br$	558-91-8	2.47	5.75
n-$C_6F_{13}Br$	335-56-8	2.74	3.52
n-$C_7F_{15}Br$	375-88-2	1.66	2.20
$BrCF_2Br$	75-61-6	0.40	
$Br(CF_2)_2Br$	124-73-2	24.00	9.21
$Br(CF_2)_3Br$	4259-29-4	2.33	1.27
$Br(CF_2)_4Br$	335-48-8	20.50	8.64
$Br(CF_2)_5Br$	24331-48-4	6.70	3.30
$Br(CF_2)_6Br$	918-22-9	5.43	1.74
$Br(CF_2)_7Br$	37819-18-4	2.48	0.67
$Br(CF_2)_8Br$	812-58-8	1.53	0.27
Unidentified (many peaks)		7.77	5.99
Nonvolatile residue[b]		12.00	40.00
Gaseous components[c]		6.00	6.00

[a] Area measurement by gas chromatographic analysis of the distillate. [b] Weight per cent of nonvolatile residue left after fractional distillation. [c] Weight per cent lost during fractional distillation.

$$CF_2{=}CF_2 \longrightarrow 2{:}CF_2$$

$$CF_2{=}CF_2 \longrightarrow CF_2{=}CF\cdot + \cdot F$$

$$Br_2 \longrightarrow 2Br\cdot$$

$$\cdot Br + nCF_2{=}CF_2 + m{:}CF_2 \longrightarrow Br(CF_2CF_2)_n(CF_2)_m\cdot \qquad n,m \geqslant 0$$

$$\begin{tikzcd} & Br(CF_2CF_2)_n(CF_2)_m\cdot \arrow[dl, "\cdot F"'] \arrow[dr, "\cdot Br \text{ or dimerize}"] & \\ \text{monobromides} & & \text{dibromides} \end{tikzcd}$$

$$\cdot F + CF_2{=}CF_2 \longrightarrow$$
$$CF_3\dot{C}F_2 + nCF_2{=}CF_2 + m{:}CF_2 + \cdot Br \longrightarrow \text{monobromides}$$

The larger amount of monobromoalkanes also indicated that more free fluorine was present during the discharge.

The electrical discharge reaction of $BrCF_2CF_2Br$ was slow. The small amount of liquid collected after prolonged discharge was essentially the starting dibromide (84%). Other products identified were $Br(CF_2)_4Br$, $CFBr_3$, $BrCF_2CFBr_2$, and a few complicated olefins. These results were in accordance with previous findings[2,3,5,6] that alkanes were more stable than olefins under similar discharge conditions. The experiment also indicated that the discharge reaction of $BrCF_2CF_2Br$ occurred to a negligible extent in the TFE/Br_2 and TFE/$BrCF_2CF_2Br$ systems.

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Experimental Section

The Electrical Discharge Cell.—The cell used was similar to that reported in the literature.[2,7] A small modification described below was necessary to introduce Br_2 (or $BrCF_2CF_2Br$) to the system. A flask fitted with a gas inlet tube and an exit tube was placed between the TFE source and the gas inlet tube of the quartz discharge cell.

Spectra.—^{19}F nmr spectra were obtained with a 56.4 MHz/sec Varian DP-60 spectrometer (shifts *vs.* $CFCl_3$ as internal standard). A Bendix time-of-flight mass spectrometer was employed to record the mass spectra at 70 eV. Infrared spectra were obtained with a Beckman IR-2 spectrophotometer.

Glpc Analyses.—Analytical chromatograms were obtained with an Aerograph (202B) using a column (0.25 in. × 24 ft) packed with 10% UC-W 98 Chromosorb G, AW, DMCS 60–80 mesh. The column temperature was programmed from 70° to 250° by setting the Variac initially at 20 V and then at 80 V immediately after sample injection. Preparative glpc was accomplished by using a Nester-Faust "Prepkro" unit equipped with a column (0.25 in. × 24 ft) packed with 30% SF-96 on Chromosorb P.

Discharge Reactions of TFE/Br_2 and TFE/$BrCF_2CF_2Br$.—Liquid bromine (or $BrCF_2CF_2Br$) was placed in a flask fitted with an inlet tube just above the liquid surface and an exit tube connected to the gas inlet tube of the discharge cell. The inlet tube of the flask was connected to a pressure-regulated (by Solenoid valve) TFE line. Bromine (or $BrCF_2CF_2Br$) was kept frozen in a Dry Ice bath until the whole system was evacuated. The Dry Ice bath was then removed and the scrubbed TFE was allowed to pass through the flask carrying a small amount of bromine vapor into the discharge cell. High-voltage electric power was then applied to the reactor. The discharge was initiated between concentric quartz electrodes of 1.5–2.0 mm gaseous gap. Pressure of the reaction was maintained by the automatically controlled valve which fed TFE to the system on demand at 260 Torr. The temperature of the halogen solution was allowed to reach 45° in order that a maximum amount of bromine be allowed to enter the discharge area. However, there seemed to be an upper limit for the bromine concentration, above which the discharge would be quenched. The electrical conditions and the results of the two reactions are summarized in Table II.

TABLE II

	TFE/Br_2	TFE/$BrCF_2CF_2Br$
TFE monomer pressure, Torr	260	260
Liquid bromine charged, g	60	
$BrCF_2CF_2Br$ charged, g		50
Operating voltage kV, rms	18.0	18.0
Frequency, kc/sec	1.4	1.4
Power, W	398	396
Time, hr	1.25	1.5
Wt of product, g	96	124
TFE consumed, g	78	77
Bromine consumed, g	42	
$BrCF_2CF_2Br$ consumed, g		50
kW-hr/lb	2.35	2.18
Br_2 content in product, %	32.63	24.29

The pale yellow liquid (50 g) from the electrical discharge of TFE/Br_2 was carefully fractionated. Gas chromatographic analysis was used to follow the components present. There were many overlapping peaks in eight fractions collected [bp 50° (760 Torr) to 68° (0.7 Torr), 41 g, 82%]. Three selected fractions [bp 50–59°, 60–75° (9 Torr), and 40–64° (0.7 Torr)] covering most of the major peaks present were further separated into individual components by preparative gas chromatography and identified by mass spectroscopy, ^{19}F nmr, and infrared (see below).

The residue, a semisolid (6 g, 12%) containing 22% Br, was shown to have terminal and internal unsaturation by ir analysis. Some branching was also observed by ^{19}F nmr analysis.

The product from the electrical discharge of TFE/$BrCF_2CF_2Br$ showed similar peaks in the gas chromatographic analysis (see Table I). Fractional distillation of the product showed the following: gaseous components, 6%; distillable fluorocarbon bromides, 54%; and residue, 40%. The residue contained 13.5% Br. Instrumental analyses indicated the presence of internal and terminal double bonds and some branching.

Monobromides.—Perfluoro-1-bromobutane had ^{19}F nmr $\mathbf{CF_2}Br$ ϕ 64.0, $\mathbf{CF_2}CF_2Br$ 118.6, $CF_3\mathbf{CF_2}$ 126.0, CF_3 81.9; mass spectrum *m/e* (rel intensity) 300, 298 (0.9, 0.6) $C_4F_9Br^+$ (parent ion), 219 (10.0) $C_4F_9^+$, 131, 129 (10.0, 7.0) CF_2Br, 100 (16.0) $C_2F_4^+$, 81, 79 (1.3, 0.9) Br^+, 69 (100.0) CF_3, 31 (38.5) CF^+.

Perfluoro-1-bromopentane had ^{19}F nmr CF_2Br ϕ 63.9, $\mathbf{CF_2}CF_2Br$ 118.0, $CF_3CF_2\mathbf{CF_2}$ 122.4, $CF_3\mathbf{CF_2}CF_2$ 126.9, CF_3 81.6; mass spectrum *m/e* (rel intensity) 350, 348 (tr) $C_5F_{11}Br^+$ (parent ion), 269 (8.0) $C_5F_{11}^+$, 131 (48.0) $C_3F_5^+$, 100 (12.0) $C_2F_4^+$, 81, 79 (2.0, 1.4) Br^+, 69 (100.0) CF_3^+, 31 (52.0) CF^+.

Perfluoro-1-bromohexane had ^{19}F nmr CF_2Br ϕ 64.1, $\mathbf{CF_2}CF_2Br$ 118.0, $\mathbf{CF_2}CF_2CF_2Br$ 122.1, $CF_3CF_2\mathbf{CF_2}$ 124.1, $CF_3\mathbf{CF_2}$ 126.9, CF_3 81.6; mass spectrum *m/e* (rel intensity) 319 (2.0) $C_6F_{13}^+$, 131 (15.0) $C_3F_5^+$, 119 (10.0) $C_2F_5^+$, 100 (3.5) $C_2F_4^+$, 81, 79 (0.4, 0.3) Br^+, 69 (100.0) CF_3^+, 31 (27.0) CF^+.

Perfluoro-1-bromoheptane had ^{19}F nmr CF_2Br ϕ 63.8, $\mathbf{CF_2}CF_2Br$ 118.2, $\mathbf{CF_2}CF_2CF_2Br$ 122.2, $\mathbf{CF_2}CF_2CF_2CF_2Br$ 123.1, $CF_3\mathbf{CF_2}$ 127.2, CF_3 81.9.

Dibromides.—Perfluoro-1,1-dibromomethane[9] had ^{19}F nmr CF_2 ϕ −6.6; mass spectrum *m/e* (rel intensity) 131, 129 (65.0, 40.0) CF_2Br^+, 81, 79 (15.0, 10.0) Br^+, 69 (100.0) CF_3^+, 50 (30.0) CF_2^+, 31 (83.0) CF^+.

Perfluoro-1,2-dibromoethane[9] had ^{19}F nmr $\mathbf{CF_2CF_2}$ ϕ 64.0; mass spectrum *m/e* (rel intensity) 260 (9.5) $BrCF_2CF_2Br$ (parent ion), 181, 179 (100.0, 71.0) $CF_2CF_2Br^+$, 131, 129 (33.0, 27.0) CF_2Br^+, 100.0 (12.0) $C_2F_4^+$, 81, 79 (25.0, 20.0) Br^+, 69 (18.0) CF_3^+, 50 (51.0) CF_2^+, 31 (56.0) CF^+.

Perfluoro-1,3-dibromopropane had mass spectrum *m/e* (rel intensity) 310 (tr) $C_3F_6Br_2^+$ (parent ion), 231, 229 (24.0, 18.0) $C_3F_6Br^+$, 131, 129 (25.0, 18.0) CF_2Br^+, 100 (17.0) $C_2F_4^+$, 81, 79 (3.0, 2.3) Br^+, 69 (40.0) CF_3^+, 50 (7.0) CF_2^+, 31 (100.0) CF^+.

Perfluoro-1,4-dibromobutane had ^{19}F nmr CF_2Br ϕ 64.0, $\mathbf{CF_2CF_2}$ 118.1; mass spectrum *m/e* (rel intensity) 360 (tr) $C_4F_8Br^+$ (parent ion), 281, 279 (30.0, 22.0) $C_4F_8Br^+$, 131, 129 (47.0, 31.0) CF_2Br^+, 119 (10.0) $C_2F_5^+$, 100 (37.0) $C_2F_4^+$, 81, 79 (11.0, 8.0) Br^+, 69 (89.0) CF_3^+, 50 (28.0) CF_2^+.

Other dibromides were assigned structures on the basis of gas chromatogram retention time and ^{19}F nmr analysis (see Table III).

TABLE III

^{19}F NMR DATA OF PERFLUORODIBROMIDES

Assigned structure	CF_2Br	$\mathbf{CF_2}CF_2Br$	$-CF_2-$	Gc[b] retention time, min
$Br(CF_2)_5Br$	64.0 (1)[a]	118.4 (1)	121.7 (0.5)	2.7
$Br(CF_2)_6Br$	63.9 (1)[a]	118.1 (1)	121.8 (1)	3.4
$Br(CF_2)_7Br$	64.1 (1)[a]	118.2 (1)	122.2 (1.5)	4.25
$Br(CF_2)_8Br$	64.0 (1)[a]	118.2 (1)	122.4 (2.0)	5.0

[a] Relative area ratios. [b] Gas chromatogram.

The retention times for other dibromides follow: $BrCF_2Br$, 1.1 min; $Br(CF_2)_2Br$, 1.3 min; $Br(CF_2)_3Br$, 1.7 min; and $Br(CF_2)_4Br$, 2.1 min.

Perfluorohexane[10] had ^{19}F nmr CF_3 ϕ 82.0, $CF_3\mathbf{CF_2}$ 128.3, $-CF_2-$ 124.3; mass spectrum *m/e* (rel intensity) 300 (3.3) $C_6F_{12}^+$ (parent ion), 250 (19.0) $C_5F_{10}^+$, 231 (54.0) $C_5F_9^+$, 169 (46.0) $C_3F_7^+$, 131 (64.8) $C_3F_5^+$, 119 (28.1) $C_2F_5^+$, 100 (38.0) $C_2F_4^+$, 69 (100.0) CF_3^+, 50 (39.8) CF_2^+.

Discharge Reaction of $BrCF_2CF_2Br$.—Forty grams of $BrCF_2CF_2Br$ was placed in a precooled flask as described previously. It was kept frozen in a Dry Ice bath until the discharge system was evacuated. The Dry Ice bath was then replaced by a hot water bath. When the vapor pressure of $BrCF_2CF_2Br$ reached 170 Torr, high voltage electric power was applied. The discharge was initiated at the operating voltage of 18 kV and at the frequency of 1.4 kcps. There was a gradual pressure buildup (170–750 Torr), which was not observed with the other two systems. After 3.5 hr of discharge, a small amount (17 g) of light brown, clear liquid was collected. Gas chromatographic analysis indicated that 84% of the liquid was the original di-

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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$_2$Br 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.

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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$_2$O 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$_2$O, 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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