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# Chlorofluorination of Carbon Disulfide and Sulfur[*1]

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Chlorofluoromethanes and sulfur hexafluoride were obtained in good yields by the electrochemical fluorination of carbon disulfide in the presence of chlorine. The yields and compositions of the products were altered by the amount of chlorine fed in during electrolysis and also by the concentration of sulfur or carbon tetrachloride dissolved in carbon disulfide. Tetrafluoromethane, trifluoromethylsulfur pentafluoride, difluoromethylene bis-(sulfur pentafluoride), bistrifluoromethyl disulfide, and chlorodifluoromethylsulfur pentafluoride were also among the products. Further, the electrochemical fluorination of elementary sulfur was accomplished by the application of the technique of chlorofluorination, and sulfur hexafluoride was obtained in a reasonable yield. The chlorofluorinations of methyl sulfide and methyl disulfide were also attempted, but they afforded only chlorotrifluoromethane in poor yields.

Much attention has been paid to the fluorination of carbon disulfide with various fluorinating agents,[1] *e.g.*, fluorine, iodine pentafluoride, cobalt trifluoride and silver fluoride. The electrochemical fluorination of carbon disulfide has also been investigated by several workers.[2] On the other hand, the treatment of carbon disulfied with, *e.g.*, antimony pentachloride in the presence of hydrogen fluoride has been established to produce chlorofluoromethanes.[3]

In the present paper, we wish to report on the chlorofluorination of carbon disulfide and sulfur by the electrochemical process, which was found to proceed quite smoothly by a method similar to one described previously.[4]

We attempted initially to fluorinate the perchloroorganosulfur compounds, including trichloromethanesulfenyl chloride.[*2] However, it was found that, upon electrochemical fluorination, these samples afforded mainly chlorofluoromethanes and sulfur hexafluoride as the cleaved products. This suggested the possible electrochemical fluorination of carbon disulfide in the presence of chlorine to obtain chlorofluoromethanes and sulfur hexafluoride. As expected, these products were obtained in good yields. In addition, their yields and compositions could be controlled satisfyingly by changing the chlorine feed rate and also by changing the composition of the substrate which was subjected to chlorofluorination.

An important feature of this halogenation is that chlorofluoromethanes and sulfur hexafluoride were simultaneously obtained in good yields from carbon disulfide. This process was applied successfully to the electrochemical fluorination of elementary sulfur. The fluorination of sulfur has previously been carried out with fluorine,[5] chlorine trifluoride,[6] and chlorine monofluoride.[7]

## Results and Discussion

The electrochemical fluorination of perhalogenoorganosulfur compounds yielded, not the expected derivatives of sulfur hexafluoride, but the cleaved products, as is indicated in the following scheme:

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[*1] Presented in part at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

1) a) E. A. Tyczkowski and L. A. Bigelow, *J. Amer. Chem. Soc.*, **75**, 3523 (1953); b) G. A. Silvey and G. H. Cady, *ibid.*, **72**, 3624 (1950); c) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, **1953**, 3219; d) H. J. Emeléus and D. E. MacDuffie, *ibid.*, **1961**, 2597.

2) G. A. Silvey and G. H. Cady, *J. Amer. Chem. Soc.*, **74**, 5792 (1952); A. F. Clifford, H. K. El-Shamy, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, **1953**, 2372.

3) Kinetic Chemical Co., Inc., U. S. 2004932 (1935); Imperial Chemical Industries Co., Ltd., Brit. 463970 (1937).

4) S. Nagase, H. Baba and T. Abe, This Bulletin, **40**, 2358 (1967).

[*2] Trichloromethanesulfenyl chloride is generally synthesized by the reaction of carbon disulfide with chlorine in the presence of iodine as a catalyst at 0°C (P. Klason, *Ber.*, **20**. 2376 (1887)).

5) K. G. Dinbich and R. W. Ray, *J. Chem. Soc.*, **1934**, 1346; B. Cohen and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 754 (1962).

6) F. Nyman and H. L. Roberts, *J. Chem. Soc.*, **1962**, 3180.

7) J. J. Pitts and A. W. Jach, *Inorg. Chem.*, **7**, 1661 (1968).

| Sample[*3] | | Products[*4] |
|---|---|---|
| $CCl_3SCl$ | $\longrightarrow$ | $CCl_2F_2$, $CClF_3$, $CCl_3F$, $CF_4$, $SF_6$ and $CHF_3$ |
| $CCl_2S$ | $\longrightarrow$ | $SF_6$, $CCl_2F_2$, $CClF_3$, $CF_4$, $CHF_3$ and $CF_3SF_5$ |
| $(CCl_2S)_2$ | $\longrightarrow$ | $SF_6$, $CClF_3$, $CCl_2F_2$, $CF_4$, $CHF_3$, $CHClF_2$ and $CF_3SF_5$ |
| $(CF_2S)_2$ | $\longrightarrow$ | $CF_4$, $SF_6$, $CHF_3$, $CF_3SF_5$ and $(CF_3)_2SF_4$ |
| $CCl_3SO_2Cl$ | $\longrightarrow$ | $SO_2F_2$, $CF_4$, $CClF_3$, $CF_3SO_2F$, $CCl_3F$ and $CCl_2F_2$ |

As contrasted with the behavior of the carbon-oxygen double bond upon electrochemical fluorination, the carbon-sulfur double bond is easier to cleave. For example, phosgene afforded the trifluoromethyl hypofluorite in about a 7% yield,[8] but from thiophosgene, the corresponding product, trifluoromethylsulfur pentafluoride was obtained in only a 1% yield, and there was no trace of thiocarbonyl fluoride. It seems that the cleavage of the carbon - sulfur bond, especially in such compounds as perhalogenoorganosulfur derivatives, occurs extensively on electrochemical fluorination and that the yields of products which retain the carbon-sulfur bond are poor.

The reaction conditions for the chlorofluorination of carbon disulfide, and for that of carbon disulfide and sulfur, are presented in Tables 1 and 2 respectively.

The results obtained with carbon disulfide and those obtained with carbon disulfide and sulfur are summarized in Table 3.

While chlorine was being absorbed in carbon disulfide, the fluorination of the resulting chlorinated compounds as well as that of unchanged carbon disulfide led to the formation of chlorofluoromethanes and sulfur hexafluoride, together with trifluoromethylsulfur pentafluoride and difluoromethylene bis(sulfur pentafluoride).

Table 1. Conditions for the chlorofluorination of carbon disulfide

Anodic current density, 2.7 A/dm²; cell voltage, 6.5—7.5 V; cell temperature, 5—6°C; He, 45 m*l*/min; carbon disulfide containing catalytic amount of iodine (0.1% by wt), 0.2 mol

| Run No. | Chlorine[*a] feed rate (m*l*/min) | Total amount of chlorine fed (mol) | Electricity passed (A·hr) |
|---|---|---|---|
| 1 | 15 | 0.22 | 129 |
| 2 | 30 | 0.44 | 132 |
| 3[*b] | 30 | 0.42 | 129 |
| 4 | 60 | 0.85 | 131 |
| 5[*c] | | | 132 |

[*a] Gas volume is expressed in normal condition.

[*b] Sodium fluoride (10 g) was added.

[*c] Carbon tetrachloride (30.8 g) was added.

Under the reaction conditions applied, chlorofluoromethanes were obtained in the highest yield (33.9%) in Run 3, in which sulfur hexafluoride was produced in a 52.8% yield. The yield of sulfur hexafluoride is a little lower than that from the electrochemical fluorination of sulfur mono- or dichloride.[9] In Run 3, the addition of sodium fluoride can be considered to have an effect on the solubilities of the fluorinated products and to result in increased amounts of the products obtained. By increasing the molar ratios (chlorine to carbon disulfide) from approximately 1 to 2, the yield of chlorofluoromethanes is increased from 5.1 to 31.7%, but a further increase in the molar ratio has no effect on the yield.

The chlorofluorination proceeded also by the

Table 2. Conditions for the chlorofluorination of carbon disulfide and sulfur

Anodic current density, 2.7 A/dm²; cell voltage, 5.1—7.1 V; cell temperature, 5—6°C; He, 45 m*l*/min; sodium fluoride, 10 g

| Run No. | Carbon disulfide[*a] fed (mol) | Sulfur fed (g) | Chlorine[*b] feed rate (m*l*/min) | Total amount of chlorine fed (mol) | Electricity passed (A·hr) |
|---|---|---|---|---|---|
| 6 | 0.20 | 6.4 | 30 | 0.43 | 129 |
| 7 | 0.20 | 6.4 | 60 | 0.86 | 129 |
| 8 | | 12.8 | 30 | 0.43 | 129 |
| 9 | | 12.8 | 60 | 0.86 | 131 |

[*a] Iodine was dissolved in it by 0.1% (by wt).

[*b] Gas volume is expressed in normal condition.

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[*3] These samples except trichloromethanesulfenyl chloride are sparingly soluble in anhydrous hydrogen fluoride, so the addition of sodium fluoride was required in order to obtain an electrical conducting solution.

[*4] The components are arranged in order of the decrease in the product composition (mol%).

8) To be published.

9) S. Nagase, T. Abe and H. Baba, This Bulletin, **42**, 2062 (1969).

TABLE 3. RESULTS WITH CHLOROFLUORINATION

| Run No. | Product obtained (g) | Total*a yield (%) | Cl-F*b methanes (%) | SF$_6$*c yield (%) | Product composition, mol% CF$_4$ | CClF$_3$ | CCl$_2$F$_2$ | CCl$_3$F | SF$_6$ | CF$_3$SF$_5$ | CF$_3$SSCF$_3$ | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 41.9 | 170.0 | 5.1 | 39.6 | 29.3 | 1.7 | 1.0 | 0.3 | 46.5 | 19.9 | 0.3 | CHF$_3$(0.8),<br>CF$_2$(SF$_5$)$_2$(0.2) |
| 2 | 46.0 | 181.7 | 31.7 | 43.5 | 29.3 | 7.1 | 7.5 | 2.8 | 47.9 | 3.9 | 1.3 | CF$_2$ClSF$_5$(0.1),<br>CHF$_3$(0.1) |
| 3 | 49.0 | 191.4 | 33.9 | 52.8 | 17.6 | 8.8 | 4.6 | 4.3 | 55.2 | 6.2 | 2.5 | CHF$_3$(0.6),<br>CF$_2$ClSF$_5$(0.2) |
| 4 | 43.8 | 176.8 | 29.0 | 43.5 | 20.9 | 6.6 | 7.2 | 2.7 | 49.2 | 9.3 | 1.9 | CHF$_3$(1.8),<br>CF$_2$ClSF$_5$(0.2),<br>CF$_2$(SF$_5$)$_2$(0.2) |
| 5 | 65.4 | 130.0 | 44.3 | 45.4 | 23.1 | 5.8 | 12.2 | 16.2 | 31.6 | 8.0 |  | CF$_2$(SF$_5$)$_2$(1.7),<br>CHF$_3$(1.0), CHClF$_2$<br>(0.3), CF$_2$ClSF$_5$(0.1) |
| 6 | 47.7 |  | 7.5 | 38.4 | 17.0 | 2.5 | 1.2 | 0.4 | 65.9 | 9.4 | 2.1 | CHF$_3$(1.5) |
| 7 | 47.7 |  | 18.7 | 38.2 | 11.4 | 4.0 | 2.7 | 3.4 | 66.2 | 8.0 | 3.4 | CHF$_3$(0.9) |

| Run No. | SF$_6$*d yield (%) | Current*e efficiency (%) |
|---|---|---|
| 8 | 37.5 | 3.3 |
| 9 | 43.2 | 8.4 |

*a The total yield={(the total moles of the products including fragmented ones)/[(the mole of carbon disulfide consumed)+(the mole of carbon tetrachloride fed)]}×100

*b Total yield of chlorofluorinated methanes; the total yield of chlorofluoromethanes={(the total moles of the chlorofluoromethanes)/[(the mole of carbon disulfide consumed)+(the mole of carbon tetrachloride fed)]}×100

*c The yield of sulfur hexafluoride={(the mole of sulfur hexafluoride)/[2×(the mole of carbon disulfide consumed)+(g·atom of sulfur fed)]}×100

*d The yield of sulfur hexafluoride={(the mole of sulfur hexafluoride)/(g·atom of sulfur consumed)}×100

*e The calculation of current efficiency was based on the amount of current assumed to be required to form fluorine with a discharging fluoride ion which would react with sulfur according to the following equation. $S+6F=SF_6$

non-electrochemical mechanism to a certain extent in anhydrous hydrogen fluoride. For example, without a passing current, chlorine was fed into anhydrous hydrogen fluoride containing carbon disulfide at the feed rate of 30 m*l*/min for 320 min (reaction conditions; $CS_2$ fed, 0.2 mol; total amount of $Cl_2$ fed, 0.43 mol; cell temp., 5—6°C); a product with the following composition (mol %) was obtained in a 40.4% yield of chlorofluoromethanes: chlorotrifluoromethane (2.0), dichlorodifluoromethane (82.0), trichlorofluoromethane (14.3), and bistrifluoromethyl disulfide (1.7).

It is interesting to note that bistrifluoromethyl disulfide was produced in these experiments. It has been reported that the fluorination of carbon disulfide with iodine pentafluoride led to the formation of bistrifluoromethyl disulfide in a good yield;[1c)] however, in the present experiment, it was derived from the hydrolytic reaction of trifluoromethanesulfenyl chloride[10)] in gas-washing bottles which is easy to produce, even without a passing current.

An increased amount of sulfur hexafluoride was obtained when carbon disulfide containing sulfur was subjected to chlorofluorination, and the yield of chlorofluoromethanes (in Runs 6 and 7) was reduced. Similarly, the co-fluorination of carbon disulfide and carbon tetrachloride yielded an increased amount of chlorofluoromethanes in Run 5, which might be considered to result in the chlorination of carbon disulfide by means of chlorine liberated from the carbon tetrachloride attacked by fluorine radical during electrolysis.

The electrochemical fluorination of elementary sulfur feeding chlorine yielded mainly sulfur hexafluoride, together with a trace of sulfur chloridepentafluoride. The conversion of sulfur hexafluoride, however, was low, and most of the starting material (finely powdered sulfur) was recovered in an aggregated state. The composition of the reaction product was nearly constant throughout the electrolysis. For example, the composition (mol%) of the products (direct analysis by G.C.) was as follows (in Run 9): $SF_6$ 77.5, $SO_2F_2$ 18.0, and $SClF_5$ 4.5. It is not clear why sulfuryl fluoride was detected in the above experiment.

The chlorofluorination of methyl sulfide and methyl disulfide was also conducted in a similar manner. The yields of chlorofluorinated compounds were, however, low, giving chlorotrifluoromethane only in yields of 0.6% and 1.1% respectively. In order to make this point clear, the fluorinations of chloromethyl sulfides were subsequently attempted. The instability of all chloromethyl sulfides, except one having a trichloromethyl group, when treated with antimony trifluoride has been reported.[14)]

In this electrochemical fluorination, similarly, $\alpha,\alpha$-dichloromethyl sulfide gave no appreciable quantities of the corresponding fluorinated products. When $\alpha,\alpha$-dichloromethyl sulfide was subjected to electrochemical fluorination (reaction conditions: sample, 0.2 mol; helium, 45 m*l*/min; anodic current density, 2.7 A/dm$^2$; electricity passed, 99.2 A·hr; cell voltage, 6—7 V; cell temp., 5—6°C), the product consisted of chlorotrifluoromethane (8.6 mol %), dichlorodifluoromethane (1.3), chlorodifluoromethane (0.6), tetrafluoromethane (31.9), trifluoromethane (11.8), sulfur hexafluoride (13.6), trifluoromethylsulfur pentafluoride (26.9), bis(trifluoromethyl)sulfur tetrafluoride (4.4), pentafluoroethylsulfur pentafluoride (0.2), and hexafluoroethane (0.7). The yield of chlorofluoromethanes was 15.7%.

When $\alpha,\alpha,\alpha$-trichloromethyl sulfide, which shows a facile halogen exchange with hydrogen fluoride, affording $\alpha,\alpha,\alpha$-trifluoromethyl sulfide, was fluorinated under the conditions described above (electricity passed, 48.3 A·hr), the composition (mol%) of the product was as follows; chlorotrifluoromethane (1.9), dichlorodifluoromethane (2.5), tetrafluoromethane (23.6), trifluoromethane (4.6), sulfur hexafluoride (5.7), trifluoromethylsulfur pentafluoride (11.3), bis(trifluoromethyl)sulfur tetrafluoride (14.9), and $\alpha,\alpha,\alpha$-trifluoromethyl sulfide (35.5). The yield of chlorofluoromethanes was 5.3%. Notably, bis(trifluoromethyl)sulfur tetrafluoride was obtained in better yields, 6.6% from $\alpha,\alpha$-dichloromethyl sulfide and 18.0% from $\alpha,\alpha,\alpha$-trichloromethyl sulfide respectively, compared to the yield (3.8%) from dimethyl sulfide.

The results may suggest that, in the chlorofluorination of methyl sulfide, the fluorination takes place with a priority to chlorination, at least at the monochloro-form stage, before chlorination proceeds further.

Thus, carbon disulfide is chlorinated by chlorine in anhydrous hydrogen fluoride, affording trichloromethanesulfenyl chloride and sulfur mono- or dichloride. The former might then proceed further to carbon tetrachloride and sulfur mono- or dichloride, or to trifluoromethanesulfenyl chloride, as a result of the easy replacement of the chlorine of the trichloromethyl group in anhydrous hydrogen fluoride, then, upon the electrochemical fluorination of part of it, carbon - sulfur bond fission occurs to give tetrafluoromethane and sulfur hexafluoride.

Sulfur is considered to be converted into a divalent state ($S_2Cl_2$ or $SCl_2$) by chlorine in the cell; subsequent fluorination yields hexavalent sulfur ($SF_6$ and $SClF_5$).

## Experimental

**Materials.** The carbon disulfide, sulfur (finely

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10) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, **1955**, 2901.

powdered, guaranteed reagent), trichloromethanesulfonyl chloride, methyl sulfide, and methyl disulfide were purchased from commercial sources, while the trichloromethanesulfenyl chloride, thiophosgene,[11] thiophosgene dimer,[12] 2,2,4,4-tetrafluoro-1,3-dithietane,[13] α,α-dichloromethyl sulfide, and α,α,α-trichloromethyl sulfide[14] were synthesisted by the methods described in the literature.

All these chemicals except sulfur were purified by conventional methods; their purity was confirmed before use by gas chromatography using a Shimadzu GC - 1C model Chromatograph and by mass spectroscopy using a Hitachi Model RMU-7.

The purity of anhydrous hydrogen fluoride was better than 99%.

**Apparatus.** The electrochemical fluorination apparatus used was almost the same as that described in previous papers.[4,15] The cell capacity was 1 *l*. The nickel electrodes consisted of a pack of alternate anodes (8 sheets) and cathodes (7 sheets). The effective surface area of the anodes was 9.2 dm$^2$. For charging the liquid samples precisely, a so-called "sample injector" was devised. It was fastened on the top of the cell with a fluoroelastomer rubber stopper. It consisted of a small tube (inlet) [8 mm od. × 5 mm id. × 3 cm length; poly(tetrafluoroethylene) resin] connected with an even smaller tube (outlet) [2 mm od. × 1 mm id. × 50 cm length; poly(chlorotrifluoroethylene) resin] which was inserted into the cell so as to reach its bottom. The inlet of the tube was covered with a silicone rubber stopper. A weighed liquid sample was led into the cell through the sample injector. The sampling valve was fitted with the line next to a sodium fluoride pellet tube for the direct analysis by GC of the evolving gaseous products from the cell.

Trap-to-trap distillation was carried out by a vacuum line technique using a series of traps (100 m*l* capacity) which were a part of a low-temperature distillation unit.

IR spectrum measurements was accomplished with a Hitachi EPI-S2 recording spectrometer, using a 6-cm gas cell equipped with two NaCl windows.

**Procedures.** As a typical example, the procedures for the chlorofluorination of carbon disulfide containing sulfur (Run 6) will be described.

Sulfur (6.4 g) was dissolved in carbon disulfide (15.2 g) while being warmed slightly, and then 15 mg of iodine was added. This mixture was introduced into anhydrous hydrogen fluoride (1 *l*) which had been purified by electrolysis. The carbon disulfide solution and anhydrous hydrogen fluoride formed two layers. The lower layer (the carbon disulfide solution) covered the bubbler located at the bottom of the cell.

Then sodium fluoride (10 g) was added in anhydrous hydrogen fluoride, and chlorine (30 m*l*/min) diluted by helium (45 m*l*/min) was directed through the bubbler into the carbon disulfide layer; the electrolysis of the solution was then carried out with an anodic current density of 2.7 A/dm$^2$, at a cell voltage of 5.9—7.1 V, and with a cell temperature of 5—6°C. The electrolysis was conducted for 129 A·hr.

The gases evolved from the cell were passed through a reflux condenser kept at −30°C, and over sodium fluoride (hydrogen fluoride absorber), and then bubbled through an aqueous solution of sodium sulfite containing a small amount of potassium iodide in consecutive Ichinose gas washers in order to eliminate oxygen difluoride, chlorine, derivatives of sulfur tetrafluoride, and sulfur chloridepentafluoride, passed through a trap cooled in ice, and finally condensed in two consecutive traps immersed in liquid nitrogen.

At regular intervals, gas was sampled from the sampling valve and was analysed directly by gas chromatography (columns and conditions: Kel F 3*[5] 30% on Chromosorb PAW, 3 m, 0°C; FC 43*[5] 66% on Celite 545 SK, 6 m, 0°C: carrier gas; He).

The composition (peak area %) of the evolved gas was, for example, $CF_4+CClF_3+CHF_3$ (47), $SF_6$ (6), $CF_3SF_5$ (8), $CCl_2F_2$ (2), $CF_3SCl$ (32), $CS_2+CCl_3F$ (5) after 60 A·hr electrolysis.

The reaction products (47.7 g) condensed in the cold traps were carefully divided into five fractions by trap-to-trap distillation.

The subsequent identification and the analysis of individual species, was accomplished by gas chromatography (column: silica gel; carrier gas : He) and IR spectrum measurements, as has been described previously.[4,9]

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[11] See *[2].

[12] A. Schönberg and A. Stephenson, *Ber.*, **66B**, 567 (1933).

[13] W. J. Middleton, E. G. Howard and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).

[14] W. E. Truce, G. H. Birum and E. T. McBee, *J. Amer. Chem. Soc.*, **74**, 3594 (1952).

[15] Preceding paper: T. Abe, S. Nagase and K. Kodaira, This Bulletin, **43**, 957 (1970).

*[5] Minnesota Mining and Manufacturing Co., Ltd.,

*[6] Trifluoromethanesulfenyl chloride (bp −1°C) was identified by employing authentic samples prepared by the reaction of bistrifluoromethyl disulfide with chlorine under the irradiation of UV light.[2c] The infrared spectrum of trifluoromethanesulfenyl chloride exhibited strong characteristic absorbtion bands ($CF_3$ stretch) at 1190 cm$^{-1}$ and 1135 cm$^{-1}$.