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# Chemical Decomposition of Chlorofluorocarbons by Reductive Dehalogenation Using Sodium Naphthalenide

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All halogen atoms in 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) were removed in the form of chloride and fluoride ions by the treatment with sodium naphthalenide (1.5 equiv. per halogen atom) in THF at 150 °C for 50 min in the presence of 10 vol% tetraethyleneglycol dimethylether. Similar treatment was also efficacious in the dehalogenation of F-22 and F-12.

It has been widely recognized that chlorofluorocarbons (CFCs) whose gross production in the world has been so inflated that the Montreal UNEP Protocol$^{1)}$ for their regulation was adopted in 1987 are strongly suspected to deplete the ozone layer in stratosphere. In this regard, not only the recovery technology but also safe and efficient destruction methods of used CFCs must be established urgently.

For safety sake of the decomposition of environmentally harmful organohalogen compounds, reductive transformation of organic halogen atoms into halide ions$^{2)}$ is more reliable and secure than the oxidative incineration process.$^{3)}$ CFCs, however, have not been regarded for safe destruction in view of environmental protection because of their chemical and physical stability. In the present report, sodium naphthalenide$^{4)}$ which was once proved to be most efficient for the reductive removal of chlorines from organochlorine compounds$^{5)}$ is shown again to be efficacious in the complete defluorination of CFCs.

While perfluoroalkanes and CFCs have generally been regarded resistant to chemical transformations,$^{6,7)}$ we recently found that poly(chlorotrifluoroethylene), PCTFE, reacts with sodium naphthalenide smoothly.$^{8)}$ This high reactivity is due to the presence of C-Cl bonds which act as the trigger of defluorination as shown in Scheme 1. This acceleration effect can be superimposed to the reductive defluorination of CFCs because of their structural similarity to PCTFE.

The dehalogenation of 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) with sodium naphthalenide in solution proceeded exothermically and, as shown in Table 1, the rate of dechlorination was very fast. For example, the dechlorination reached 97 - 98% in the reaction with an equivalent amount of the reagent (reductant/halogen = 1.0) for 10 min at 0 °C (entry 1).

Table 1. Dehalogenation of Freon 113 by sodium naphthalenide in THF solution a)

| No. | Solvent b) | Amount of reductant (e$^-$/F-113) | Reductant concentration M | Additive b) (vol %) | Temp °C | Time min | Dehalogenation % Cl$^-$ | F$^-$ |
|---|---|---|---|---|---|---|---|---|
| 1 | THF | 6 | 0.4 | - | 0 | 10 | 98 | 46 |
| 2 | THF | 6 | 0.4 | - | 0 | 400 | 98 | 67 |
| 3 | THF | 12 | 0.4 | - | 0 | 400 | 100 | 93 |
| 4 | THF | 12 | 0.4 | - | 40 | 100 | 99 | 88 |
| 5 | THF | 12 | 0.4 | - | 40 | 400 | 99 | 99 |
| 6 | THF | 9 | 1.2 | ME-4(10) | 100 | 50 | 100 | 89 |
| 7 | ME-2 | 9 | 1.2 | - | 100 | 50 | 100 | 83 |
| 8 | ME-2 | 12 | 1.2 | - | 100 | 50 | 100 | 93 |
| 9 | THF | 9 | 1.2 | ME-4(10) | 150 | 50 | 100 | 98 |
| 9' | THF | 9 | 1.2 | ME-4(10) | 150 | 50 | 99 | 100 |
| 10 | THF | 9 | 1.2 | HMTA(10) d) | 150 | 50 | 99 | 97 |
| 11 | THF | 9 | 1.2 | - | 150 | 50 | 100 | 86 |

a) Reaction scale: 0.937 g (5 mmol) of F-113 in 20 mL of THF was added to a THF solution of the reductant. b) THF: tetrahydrofuran; ME-2 or ME-4: di- or tetraglyme; HMTA: hexamethylenetetramine. c) Determined by ion chromatography. d) Mol %.

Table 2. Dehalogenation of gaseous Freons 113, 22, and 12

| No. | Amount of reducant (e$^-$/Freon) | Bubbling N$_2$ (mL/min) | Bubbling Time min | Additive (vol %) | Time a) min | Temp °C | Dehalogenation /% Cl$^-$ | F$^-$ | F-113 not absorbed % |
|---|---|---|---|---|---|---|---|---|---|
| F-113 | | | | | | | | | |
| 1 | 11.6 | 50 | 2.3 | - | 5 | 0 | 98 | 49 | 0.1 |
| 2 | 6.5 | 100 | 2.0 | - | 5 | 0 | 95 | 45 | 0.7 |
| 3 | 6.5 | 200 | 1.0 | - | 5 | 0 | 96 | 52 | 1.3 |
| F-22 | | | | | | | | | |
| 4 | 6 | - | 5.0 | - | 50 | 20-150 | 99 | 81 | |
| 5 | 6 | - | 5.0 | ME-4(10) | 50 | 20-150 | 100 | 89 | |
| 6 | 6 | - | 5.0 | ME-4(20) | 50 | 20-150 | 100 | 100 | |
| F-12 | | | | | | | | | |
| 7 | 6 | - | 5.0 | - | 50 | 20-150 | 100 | 73 | |
| 8 | 8 | - | 5.0 | ME-4(10) | 50 | 20-150 | 100 | 97 | |

a) Freon gas was bubbled into the reductant solution at 20 °C and then the temperature was raised to 150 °C.

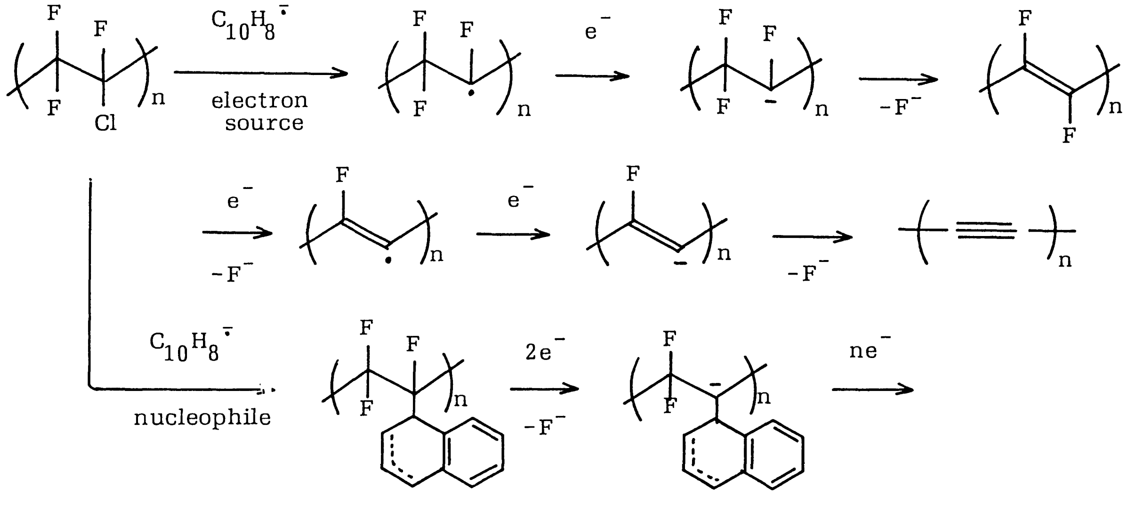
On the other hand, the rate of defluorination is puzzling because about 50% of fluorine atoms was removed almost as easily as chlorine atoms but the removal of the remaining fluorine atoms became difficult. Prolonged treatment with 2 equiv. of the reductant for 400 min attained 93% defluorination (entry 3).

At 40 °C the defluorination rate was accelerated significantly. A prolonged treatment for 400 min with 2.0 equiv of the reductant finally attained the expected defluorination $>$99% (entry 5). With the purpose of shortening the time within one hour, the temperature was raised to 100 and 150 °C. Some additives which are expected to increase the reduction power of naphthalenide by facilitating the dissociation of reductant ion pairs were examined (entries 6, 9, 10). At 150 °C in THF with 1.5 equiv. of the rductant in the presence of 10 vol% tetraglyme the defluorination finally reached 100% (entry 9'). Hexamethylenetetramine was also proved to be an effective additive. Thus, the requisite of shortening the time for practical application of the present method was attained.

On the assumption that CFCs will be supplied as gases, we examined their absorption into sodium naphthalenide solution and the dehalogenation which follows. A controlled $N_2$ stream was bubbled in a container of F-113 which was warmed to 30 °C. The vaporized F-113 was led to a THF solution of the reductant cooled to 0 - 5 °C. The outlet from the reactor was led to a liquid $N_2$ trap, but no appreciable amount of unreacted F-113 nor reduction intermediates were detected. This indicates that F-113 in nitrogen stream was efficiently absorbed probably by a diffusion-controlled reaction.[9)] In Table 2 some results are shown: within a short time (5 - 8 min) the defluorination reached the degree of 44 - 52% while dechlorination was over 95%. Therefore, a gaseous waste F-113 can be absorbed in the reductant solution followed by heating in a closed system.

Chlorodifluoromethane (F-22) and dichlorodifluoromethane (F-12), as the typical gaseous CFCs, were measured by a gas-burrette and absorbed in a THF solution of the reductant at 20 °C. The solution was heated at 150 °C for 50 min in a stainless steel cylinder. Results are shown in Table 2. As for the treatment of F-22 with 1 equiv. of the reductant for a short period, the defluorination reached only 66% though the dechlorination was 100%. However, when 20 vol% of tetraglyme was added together with 2 equiv. of the reductant, the defluorination was almost complete (entry 6). Similarly, the treatment of F-12 with 2 equiv. of the reductant at 150 °C for 50 min in the presence of 10 vol% of tetraglyme yielded 97% defluorination (entry 8).

In the application of the present method to practical purposes, solvents and naphthalene can be recovered by distillation. After removing sodium fluoride and chloride by washing with water, the organic residue does not contain halogens, thus rendering us a safe and simple incineration process.[10)] Despite of the economical disadvantage due to the stoichiometric consumption of sodium metal, characteristic advantages of the present method are safety and its easy applicability to a small scale, rapid, and on-site destruction where the cost is not so serious. Further research for practical purposes is underway.



Scheme 1. A possible reductive dehalogenation pathway of PCTFE.

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