75. *Oxidation of Polyhalogeno-compounds. Part III.*[1] *Thermal Oxidation of Some Chlorofluoroethanes.**

By R. N. Haszeldine and F. Nyman.

Thermal oxidation with molecular oxygen of the compounds $CF_3{\cdot}CHCl_2$ and $CF_3{\cdot}CH_2Cl$ in presence of chlorine as initiator gives trifluoroacetic acid in high yield. The compound $CF_3{\cdot}CCl_3$ is more stable and its oxidation is accompanied by complete carbon–carbon bond fission.

PHOTOCHEMICAL oxidation of the chlorofluoroethane $CF_3{\cdot}CCl_3$, $CF_3{\cdot}CHCl_2$, or $CF_3{\cdot}CH_2Cl$ gives high yields of trifluoroacetic acid or trifluoroacetyl chloride.[1] A free-radical reaction scheme was proposed in which the primary step is either photochemical homolysis of a carbon–halogen bond or abstraction of a hydrogen atom by one of chlorine. The thermal oxidation of these compounds, alone or in the presence of chlorine, has now been studied, since if the primary steps are the same as in the photochemical reactions it should be possible to achieve controlled oxidation to trifluoroacetic acid or its precursors. Thermal oxidation would be more convenient than photochemical oxidation for large-scale preparation of trifluoroacetic acid. The results obtained show that 1-chloro-2 : 2 : 2-trifluoroethane and 1 : 1-dichloro-2 : 2 : 2-trifluoroethane give good yields of trifluoroacetic acid. Typical results are summarised in the annexed Table.

The thermal stability of trifluoroacetic acid and trifluoroacetyl chloride in the presence of oxygen, with or without chlorine as sensitiser, was investigated to determine the temperature limitations of a successful thermal oxidation. Trifluoroacetic acid was stable in the presence of oxygen at 200° for up to 24 hr., but at 250° it begins to afford carbon dioxide by oxidation and silicon tetrafluoride by attack on the glass reaction vessel. The addition of chlorine did not decrease the thermal stability of the acid at 200°. The absence of chlorotrifluoromethane from the product showed that chlorinolysis of the acid or decomposition *via* trifluoroacetyl hypochlorite was not occurring; chlorotrifluoromethane is stable under the conditions used.

$$CF_3{\cdot}CO_2H \xrightarrow{Cl_2} CF_3Cl + CO_2 + HCl$$

$$CF_3{\cdot}CO_2H \xrightarrow{Cl_2} HCl + CF_3{\cdot}CO_2Cl \longrightarrow CF_3Cl + CO_2$$

Trifluoroacetyl chloride in the presence of oxygen at 200° was only slightly oxidised during 24 hr.; at 250° slow breakdown to carbon dioxide and silicon tetrafluoride was apparent, but trifluoroacetyl chloride was more stable than trifluoroacetic acid at this temperature.

1 : 1 : 1-Trichlorotrifluoroethane did not react with oxygen below 350°, and at 400°

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was slowly oxidised to carbon dioxide. The addition of chlorine did not lower the initiation temperature or alter the rate of oxidation. Trifluoroacetyl chloride, if formed, would itself be completely oxidised at 400° under the conditions used, and hence it cannot be deduced directly that the thermal oxidation follows the same path as that proposed earlier for the photochemical oxidation of this ethane. However, the results obtained with the other chlorofluoroethanes suggest that trifluoroacetyl chloride is again the intermediate.

Thermal oxidation of $CF_3{\cdot}CO_2H$, $CF_3{\cdot}COCl$, $CF_3{\cdot}CCl_3$, $CF_3{\cdot}CHCl_2$, *and* $CF_3{\cdot}CH_2Cl$.

Compound oxidised	Mmoles cpd. taken	Mole ratio O_2 : Cpd.	Mole ratio Cl_2 : Cpd.	Pressure (atm.)	Temp. (c)	Reaction time (hr.)	Oxidation (%)	$CF_3{\cdot}CO_2H$ yield or recovery *	
								Mmole	%
$CF_3{\cdot}CO_2H$	4·76	1·0	—	2·1	200	24	9	4·35	91
$CF_3{\cdot}CO_2H$	4·27	1·0	0·7	2·3	200	24	9 [a]	3·88	91
$CF_3{\cdot}CO_2H$	3·97	1·0	—	1·7	250	23	100	0	0
$CF_3{\cdot}CO_2H$	4·20	1·1	—	2·1	250	8	35	2·72	65
$CF_3{\cdot}COCl$	3·88	1·2	—	1·6	200	24	7	3·62 ($CF_3{\cdot}COCl$)	93
CFC·OCl	6·01	1·7	—	3·4	250	24	53	2·85 ($CF_3{\cdot}COCl$)	47
$CF_3{\cdot}CCl_3$	2·52	1·8	—	2·5	400	43	39 [b]	0	0
$CF_3{\cdot}CCl_3$	2·94	1·4	2·4	4·2	400	48	44 [a, b]	0	0
$CF_3{\cdot}CH_2Cl$	4·35	1·1	—	1·9	200	24	0	0	0
$CF_3{\cdot}CH_2Cl$	4·35	1·1	—	1·9	250	23	42 [a, b]	0	0
$CF_3{\cdot}CH_2Cl$	4·25	1·1	1·1	2·9	250	23	100 [a]	0·66	16 [c]
$CF_3{\cdot}CH_2Cl$	6·15	1·0	1·0	3·6	200	23	93 [a]	1·76	31 [d]
$CF_3{\cdot}CH_2Cl$	4·25	1·1	0·2	1·9	200	12	25 [a]	0·77	72 [e]
$CF_3{\cdot}CHCl_2$	4·76	1·0	0·1	2·1	200	23	22 [a]	0·97	93 [e]

* CO_2 and SiF_4 produced in every experiment.

[a] Products shaken with mercury to remove chlorine before distillation. [b] Thin film of unidentified white solid on wall of tube. [c] $CF_3{\cdot}CCl_3$ (1·63 mmole) formed in 38% yield; HCl produced. [d] $CF_3{\cdot}CHCl_2$ (0·88 mmole) formed in 15% yield; $CF_3{\cdot}CCl_3$ (1·76 mmole) in 31% yield; HCl produced. [e] HCl also produced.

1-Chloro-2 : 2 : 2-trifluoroethane and oxygen did not react at 200°, and at 250° slowly gave carbon dioxide and silicon tetrafluoride. The rate of oxidation of this ethane at 250° is slower than that of trifluoroacetic acid, so that the absence of the acid from the products is not surprising. When 1-chloro-2 : 2 : 2-trifluoroethane was oxidised in the presence of an equimolar amount of chlorine, reaction took place at a lower temperature, 200°, and a 31% yield of trifluoroacetic acid was obtained. The low yield of acid was primarily due to the concurrent thermal chlorination of the ethane to give 1 : 1-dichloro-2 : 2 : 2-trifluoroethane and 1 : 1 : 1-trichlorotrifluoroethane. Reduction of the amount of chlorine eliminated the unwanted chlorination, and the yield of trifluoroacetic acid increased to 72%. The lower yield (16%) of trifluoroacetic acid accompanying complete oxidation at 250° in the presence of chlorine is clearly caused by the breakdown of the acid. The action of chlorine as sensitiser is clearly to abstract hydrogen to produce the $CF_3{\cdot}CHCl$ radical, which is then rapidly oxidised as outlined in Part II.

$$CF_3{\cdot}CH_2Cl + Cl{\cdot} \longrightarrow CF_3{\cdot}CHCl{\cdot} + HCl$$

$$CF_3{\cdot}CHCl{\cdot} \xrightarrow{O_2} CF_3{\cdot}COCl, \text{ etc.}$$

The oxidation of 1 : 1-dichloro-2 : 2 : 2-trifluoroethane at 200° in the presence of a small amount of chlorine was even more successful and gave a 93% yield of trifluoroacetic acid. This yield is comparable with the 90% from photochemical oxidation in the presence of chlorine.[1] The chlorine again initiates reaction by hydrogen abstraction to give the $CF_3{\cdot}CCl_2{\cdot}$ radical, shown earlier to be readily oxidised to trifluoroacetyl chloride.

The main difference between the thermal and the photochemical oxidation of 1-chloro- and 1 : 1-dichloro-2 : 2 : 2-trifluoroethane is that the thermal reaction, even in presence of chlorine as initiator, gives only trifluoroacetic acid and not trifluoroacetyl chloride, whereas the photochemical reaction gives mainly the acyl chloride. A further difference is the importance of using small amounts of chlorine as initiator in the thermal reaction if chlorination to 1 : 1 : 1-trichlorotrifluoroethane, not observed in the photochemical experiments, is to be avoided; the rates of thermal chlorination and oxidation are presumably very similar.

Thermal oxidation of the chlorofluoroethanes, which in other respects are extremely stable chemically, can thus be achieved in simple apparatus and adapted to large-scale production of trifluoroacetic acid with a yield which, though already high, could clearly be enhanced by detailed study of the reactant ratios, temperature, pressure, initiator concentration, use of flow system, etc. The results also reveal that controlled thermal oxidation is a powerful method for the conversion of stable fluorine compounds into useful compounds containing functional groups.

EXPERIMENTAL

General Techniques.—The oxidations were carried out in sealed, 200-ml. Pyrex tubes, filled by condensation from an apparatus for manipulation of volatile compounds *in vacuo.* Oxygen was condensed into the reaction tube from a reservoir attached to the vacuum-system. All reactants were distilled before use and were analytically and spectroscopically pure. The volatile reaction products were transferred to the vacuum-system for distillation and were analysed and identified by b. p., molecular weight, vapour pressure, infrared spectroscopy, etc. Trifluoroacetic acid was often converted into its silver salt for analysis. Yields are based on material consumed. Relevant results, summarised in the Table, are from typical experiments.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 18th,* 1958.]