upon warming at high pH to give nitrite and nitrous oxide. Decomposition is progressively more rapid with decreasing pH, and nitric oxide begins to appear as a decomposition product at a pH less than 7. In strongly acid solution the product is nearly exclusively NO. Three experiments were carried out in which $Na_2N_2O_3$, dissolved in 1.5% H_2O^{18}, was decomposed under conditions such that the predominant products were NO_2^- and N_2O; in none of these was appreciable O^{18} enrichment observed in the N_2O. A separation from possible NO contamination was made by pumping at $-137°$ (melting point of s-butyl chloride).

Since nitric oxide is stoichiometrically the anhydride of nitrohydroxylamic acid, and nitric oxide solution has even been assumed[6] to contain this acid, the decomposition of $Na_2N_2O_3$ to form NO at low pH is of particular interest, but difficulties have been encountered in the mass spectrometry of NO. This decomposition and the exchange of oxygen between NO and water will be treated in a later communication.

The authors wish to express their appreciation to Mr. A. P. Irsa for mass spectrometric analyses and to Dr. R. W. Stoenner for chemical analyses.

(6) M. L. Nichols and C. W. Morse. *J. Phys. Chem..* **35**. 1239 (1931).

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The Chlorination of 1,1-Difluoroethane and 1-Chloro-1,1-difluoroethane[1]

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It has been found that iron exerts a profound influence upon the thermal chlorination of chlorofluorocarbons. Below the temperatures normally required for the chlorination and thermal dehydrochlorination of chlorofluoroethanes, both extensive dehydrofluorination and exhaustive chlorination were found to occur in the presence of iron.

McBee, *et al.*,[2] have reported that attempts at thermal chlorination of 1-chloro-1,1-difluoroethane in Pyrex above 420° resulted in considerable dehydrochlorination. This effect was less extensive at 420° than at 495°. Calfee and Smith[3] found that the chlorinolysis of polychloro 1,1-difluoroethanes at 750–850° produces some tetrachloroethylene, formed by dehydrofluorination during the chlorination stage of the process. Calfee and Florio[4] found that 1,1,1,2-tetrachloro-2,2-difluoroethane was the principal product of the chlorination of 1,1-difluoroethane between 400 and 550°, but stated that the lower temperature was necessary to obtain sub-

(1) This paper is based on work performed for the Atomic Energy Commission. by Carbide and Carbon Chemicals Company. Union Carbide and Carbon Corporation. Oak Ridge. Tennessee. Presented at the Southeastern Regional Meeting. American Chemical Society. Atlanta. Georgia. October 16. 1950.

(1a) Pennsylvania Salt Mfg. Co.. Philadelphia 18. Pa.

(2) E. T. McBee, *et al.. Ind. Eng. Chem..* **39**. 409 (1947).

(3) J. D. Calfee and L. B. Smith. U. S. Patent 2.459.767 (issued January. 1949).

(4) J. D. Calfee and P. A. Florio. U. S. Patent 2.469.290 (issued May. 1949).

stantial yields. In both the latter two references, photo-activation was employed during the early portion of the process to ensure the introduction of at least one chlorine into the molecule before a higher temperature was employed to complete the chlorination or chlorinolysis.

Experimental

1,1-Difluoroethane and 1-chloro-1,1-difluoroethane as supplied by General Chemical Company and commercial Matheson chlorine were used.

Thermal Chlorination of 1-Chloro-1,1-difluoroethane.—Iron, stainless steel, monel, nickel and copper reactors, formed from a 16″ length of 1″ pipe, were used. These were packed with some finely-divided form of the metal, leaving a free space of 85%. Heat was supplied by a 14″ electrical tube furnace, and temperatures were measured by a thermocouple attached to the reactor at the center of the reaction zone.

The chlorine and chlorodifluoroethane were passed through calibrated rotameters into the heated reactor for the desired length of time, and the products were condensed in Dry Ice–trichloroethylene traps. The liquid and solid product remaining after warming these traps to room temperature was washed with sodium carbonate solution and water, dried, and distilled.

In an iron reactor at a temperature of 200°, and using a contact time of 2 sec., based on the reactants at room temperature, 100 g. of 1-chloro-1,1-difluoroethane gave 72 g. of liquid and solid product of the following composition: CH_2ClCCl_2F, 30%; CCl_3CClF_2, 15%; CCl_3CCl_2F, 10%; and C_2Cl_6, 40%. At 300° and a contact time of 15 g. of product was obtained, composed of 5% CCl_3CCl_2F, 45% $CCl_2=CCl_2$ and 45% C_2Cl_6. At 300° and 3 sec. contact time, a stainless steel reactor gave 68 g. of product, made up of 10% CCl_3CClF_2, 35% $CCl_2=CCl_2$, 5% CCl_3CCl_2F and 45% C_2Cl_6. Under the same conditions a monel reactor yielded 46 g. of product containing 5% $CH_2ClCCl_-F_2$. 20% $CCl_2=CClF$, 25% CH_2ClCCl_2F, 20% CCl_3CClF_2, 20% $CCl_2=CCl_2$, 5% CCl_3CCl_2F and a trace of C_2Cl_6. At temperatures up to 400°, nickel and copper reactors gave less than 2 g. of product for each 100 g. of 1-chloro-1,1-difluoroethane passed through.

The Photochemical Chlorination of 1,1-Difluoroethanes.—The reactor employed for this type of chlorination consisted of a 2-l., 3-neck Pyrex flask mounted in a thermostatically-controlled aluminum-lined box. The inlet tubes extended into the flask through the side necks and were bent so as to mix the chlorine and fluoroethane at the bottom of the flask. The exit gases were withdrawn from the center neck in which a thermocouple well was sealed. Heat and light generally were supplied by two 500-w., 115-v., incandescent bulbs; but when an ultraviolet source was used, heat was supplied by two electrical resistance heaters totaling 900 w.

The effluent gases received the same treatment as did the products of the thermal chlorination.

Since the reactor had a fixed volume, and a constant rate of flow of the fluoroethane was used, the contact times varied inversely with the chlorine-to-fluoroethane ratio. The extent of this variation may be seen in Table I, which gives the results obtained by this method. Table II shows the effect of temperature changes when an ultraviolet light source was used.

Discussion

At temperatures below 400°, no appreciable reaction occurred between 1-chloro-1,1-difluoroethane and chlorine in copper and nickel reactors, nor was there any reaction detected in the dark in the Pyrex reactor up to 225°. However, the presence of an iron-containing metal exerted a profound influence upon the thermal chlorination. In contrast to the normal thermal reaction of dehydrochlorination which has been reported for chlorofluoroethanes,[2,5] extensive dehydrofluorination was

(5) P. Torkington and H. W. Thompson. *Trans. Faraday Soc..* **41**. 236 (1945): J. D. Park. *et al.. Ind. Eng. Chem..* **39**. 354 (1947): C. W. Huskins and P. Tarrant. "Preparation and Reactions of Certain Fluorochloroethylenes." Report to Office of Naval Research under contract N8onr508, June 15. 1949.

TABLE I

CHLORINATION OF CH_3CHF_2 AND CH_3CCIF_2 AS A FUNCTION
OF CHLORINE CONCENTRATION

Temperature, 200°. Illumination, two 500-w. incandescent
bulbs

Run	$Cl_2/$ ethane	Contact time,[a] min.	Yield,[b] g.	Conversion, %	CHCl₂- CHF₂	CH₂- ClC- ClF₂	CHCl₂ CClF₂	CCl₂- CClF₂
				Feed: CH_3CHF_2				
1	8.0:1	0.6	122	41				95
2	4.5:1	1.0	117	39				95
3	1.9:1	1.6	65	25	6	13	18	63
4	1.0:1	2.2	20	10	12	50	30	8
				Feed: CH_3CClF_2				
5	3.8:1	1.1	80	40		5	10	85
6	1.6:1	1.8	71	36		7	13	80
7	1.0:1	2.2	63	31		10	16	74

[a] Based on reactants at 25°. [b] Grams of product boiling
above room temperature per 100 g. of fluoroethane.

TABLE II

CHLORINATION OF CH_3CClF_2 AS A FUNCTION OF TEMPERATURE

Illumination, one G. E. H-4 100-w. ultraviolet source

Run	Mole ratio Cl_2/ethane	Temp., °C.	Yield,[a] g.	CH_2Cl- CClF₂	$CHCl_2$- CClF₂	CCl₂- CClF₂
1	6:1	125	19	11	18	70
2	5:1	175	38	8	12	80
3	5:1	200	55	6	14	80

[a] G. of product boiling above room temp. per 100 g. of
chlorodifluoroethane.

found to occur in iron reactors at 200–400°, and the
over-all reaction was that of the chlorination of
1-chloro-1,1-difluoroethane and its dehydrofluorination products, with the latter predominating.

Thus the conclusion may be drawn that iron(III)
chloride is a specific catalyst for both dehydrofluorination and chlorination of 1-chloro-1,1-difluoroethane below the temperatures which McBee[2]
found caused dehydrochlorination. Also, the effect
of the iron concentration in the metal is easily seen.
At 300° about 60% of the original fluorine was in
the products obtained with the monel reactor,
about 20% in those from the stainless steel, and
only 10% in those from the iron reactor. The
reaction initiates in each of the metals at about
200–225°, and becomes appreciable by 250°.
Iron and stainless steel reactors cannot be used
above the boiling point of iron(III) chloride, about
318°, but monel may be used to above 400°, where
the reaction becomes uncontrollable.

Nitrogen dilution of the reactants modified the
reaction somewhat, allowing the production of a
slightly greater percentage of fluorine-containing
material.

No evidence of dehydrofluorination was found
during photochemical chlorination at temperatures below 200°, and the reaction gave the expected products. The temperature necessary for
the initiation of the reaction was about 125°, and
at 200° conversions greater than 40% were effected
at one pass. In addition, chlorination at these
temperatures gave appreciable amounts of di-
and trichlorodifluoroethanes which are not obtained
at higher temperatures.

No attempt was made to determine the amount
of 1-chloro-1,1-difluoroethane formed when 1,1-
difluoroethane was the starting material, as one
preliminary distillation of the gaseous products
indicated that very little 1,1-difluoroethane was
unreacted. As when 1,1-difluoroethane was subjected to chlorine in direct sunlight,[6] no evidence
has been found of any 2-chloro-1,1-difluoroethane,
but small amounts of 2,2-dichloro-1,1-difluoroethane appeared when low chlorine-to-fluoroethane
ratios were used.

By comparison of run 5, Table I, and run 3,
Table II, it may be seen that only slight differences
exist in the composition of the products obtained
when using visible and ultraviolet light. A slightly
lower yield was obtained in the illumination from
the 100-w. ultraviolet source than in that from the
two 500-w. incandescent bulbs.

(6) A. L. Henne, J. B. Hinkamp and W. J. Zimmerschied, THIS JOURNAL, 67, 1906 (1945).

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The Preparation of Specific Adsorbants

BY SIDNEY A. BERNHARD[1]

The preparation of specific adsorbants was first
described by Dickey.[2] These adsorbants were silica gels, which, depending on the method of preparation, preferentially adsorbed a particular dye in
the series methyl, ethyl, n-propyl and n-butyl orange (I).

$$R_2N-\langle\!\!\bigcirc\!\!\rangle-N=N-\langle\!\!\bigcirc\!\!\rangle-SO_3^-$$

I. R = methyl, ethyl, n-propyl or n-butyl

Emmett[3] repeated the measurements on samples
of Dickey's gels which had been prepared seventeen months previously, and found evidence for
specificity although the effects were much smaller,
presumably as a result of the change in properties
of the gels on standing.

Experimental

In the present investigation, gels were prepared by mixing
30 ml. of aqueous sodium silicate (d 1.401) and 0.2 g. of
dye and diluting to 200 ml. To this mixture, 200 ml. of 0.2
N hydrochloric acid was added.[4] The preparations were
allowed to sit at room temperature for eight days. (Gelation occurred on the fifth day.) The gels were then poured
onto paper towels and dried in air for another eight-day
period. The dried gels were ground and sieved, and the
fraction between 60 and 200 mesh was continuously extracted with methanol at room temperature for three days.
Although most of the dye was thereby removed, some coloration of the gel persisted. Subjecting the gels to extraction
for a two-week period did not significantly diminish the in-

(1) American Cancer Society Postdoctorate Fellow, 1951–1952.
(2) F. H. Dickey, Proc. Nat. Acad. Sci., 35, 227 (1949).
(3) P. H. Emmett, private communication.
(4) Hydrochloric acid was found to give consistently better results
than acetic acid. This has been independently discovered by Dickey
(private communication). In one case, the dye (II) was added to the
hydrochloric acid rather than the silicate solution. The sodium silicate dilution reported here is relatively high. A priori, it seemed that
a high dilution and hence a slow gelation would be favorable for strong
adsorption of the dye. Recent experiments seem to indicate the contrary.