petted into the flask, the mixture was made up to volume, well shaken and replaced in the thermostat (25 ± 0.05°). The esters react slowly enough to make this procedure possible. At suitable intervals 10-ml. samples were withdrawn, added to 10 ml. of $N/15$ hydrochloric acid, and the excess acid was back-titrated with $N/20$ sodium hydroxide. In the case of the less soluble esters 10 ml. of alcohol was added before the final titration, in order to keep the organic material in solution. Failure to do so resulted in erratic end-points. The indicator was brom thymol blue (5 drops) and the end-point was matched against the color of 5 drops of indicator in 15 ml. of a $M/30$ sodium benzoate solution and 15 ml. of 50% alcohol. A 10-ml. microburet, graduated in 0.02 ml., was used for all titrations. Rate constants were calculated from the bimolecular equation for equal concentrations. There was a slight downward drift of the rate constants in the early parts of the runs and samples were usually withdrawn between 20 and 70% reaction. In a few runs cresol red was used as an indicator. The end-point was sharper, but an indicator blank had to be applied. The results of two typical determinations are recorded in Table III, and in Table IV are listed the results of all the runs.

(b) **In Acetone**[8] (E.A.B. and B.N.).—A stock solution (3 liters) of aqueous acetone was prepared by diluting 400 ml. (or 800 ml.) of carbonate-free water in a 1-l. (or 2-l.) volumetric flask to volume with purified acetone, both solvents having been thermostated. A density determination showed the stock solution to contain 55.86% by weight acetone. The solution containing the sodium hydroxide for the hydrolysis was prepared daily. Eighty ml. of $N/4$ sodium hydroxide was pipetted into a 200-ml. volumetric flask and diluted to volume with pure acetone. The normality of this solution was frequently checked, and was found to agree with that calculated on the basis of the initial concentration of sodium hydroxide. About 0.05 mole of ester, corresponding exactly to the normality of the sodium hydroxide solution, was transferred quantitatively with the acetone–water solvent to a 100-ml. volumetric flask. Fifty ml. of the 0.1 N sodium hydroxide solution was added, the flask was filled up to volume with aqueous acetone, rapidly shaken and replaced in the thermostat. Zero time was taken as half the delivery time of the sodium hydroxide solution. The sampling was carried out as described above for the runs in alcohol. Five drops of cresol red were used as indicator. Except for the unsubstituted and the *p*-methyl compounds, 10 ml. of acetone was added before titration, because otherwise the organic material precipitated in part during the titration and the end-point was not sharp. The additional acetone did not change the end-point since the same constant was obtained for ethyl *p*-methylbenzoate with and without the addition of acetone. Two typical runs are listed in Table III and the summary of all kinetic runs in Table IV.

Acknowledgment.—The help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation is gratefully acknowledged.

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NOTES

Non-exchange of Oxygen between Water and Some Compounds of Nitrogen[1]

BY FRANCIS BONNER[2] AND JACOB BIGELEISEN

RECEIVED APRIL 8, 1952

It has been shown[3] that nitrous oxide undergoes only negligible exchange of oxygen atoms with water of initially neutral *p*H. In the present investigation attempts were made to detect oxygen exchange between water and nitrous oxide, water and hyponitrite ion, and water and nitrohydroxylamite ion over a wider range of *p*H.

Two experiments were carried out in which nitrous oxide was shaken with O^{18}-enriched water (1.5% O^{18}) for 40 hours at 22°. In one experiment the water was made strongly alkaline by reaction with sodium metal; the other experiment was carried out in 1.75 N H_2SO_4. After 40 hours no enrichment as large as 0.1% in the O^{18} content of the N_2O was detectable with a Consolidated-Nier "Isotope Ratio" mass spectrometer. From these measurements, a lower limit to the half-time for the exchange of ten years is calculated.

To check further on the relation between N_2O and hyponitrous acid, exchange of oxygen between sodium hyponitrite and water was attempted at various *p*H's. Anhydrous sodium hyponitrite was prepared by the method of Partington and Shah,[4] in which sodium nitrite is reduced by sodium amalgam. The product formed showed all the characteristic chemical properties of hyponitrite; flame photometric analysis of the solid product indicated 41.7% sodium, compared with a calculated value of 43.4%. Appreciable exchange times with water were possible only at relatively high *p*H's in air, since $Na_2N_2O_2$ solutions decompose rapidly *in vacuo* and under any conditions at *p*H 7 or less. Five experiments were carried out in which $Na_2N_2O_2$ was decomposed in 1.5% H_2O^{18} solution at initial *p*H's ranging from 0.05 to 10.6. The longest exchange time in the series was 16 hours at the highest *p*H. In no case was appreciable O^{18} enrichment found in the resultant purified N_2O by mass spectrometric analysis. It is concluded that neither hyponitrous acid nor hyponitrite ion exchanges oxygen atoms with water.

Oxygen exchange was also looked for in the decomposition of aqueous sodium nitrohydroxylamite solutions. $Na_2N_2O_3$ was prepared according to the method reported by Yost and Russell,[5] in which the salt is precipitated from alcoholic solution of sodium ethoxide following the interaction of hydroxylamine and ethyl nitrate. Gravimetric analysis of the product indicated 35.7% sodium, compared with a calculated percentage of 37.6. Aqueous solutions of this compound decompose

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(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) Department of Chemistry, Brooklyn College, Brooklyn 10, N. Y.

(3) L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, **18**, 1325 (1950).

(4) J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2071 (1931).

(5) D. M. Yost and H. Russel, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 57.

upon warming at high *p*H to give nitrite and nitrous oxide. Decomposition is progressively more rapid with decreasing *p*H, and nitric oxide begins to appear as a decomposition product at a *p*H 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 *p*H 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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RECEIVED APRIL 10, 1952

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 substantial 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 3 sec., 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% $CH_2ClCClF_2$, 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

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[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).

[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.