

Experimental

Starting Materials.—Chloromaleic anhydride was supplied by the Allied Chemical and Dye Corporation and was redistilled before use, b. p. 89° (14 mm.), n_D^{20} 1.5021. *n*-Propanol, *n*-butanol and *n*-pentanol were refluxed with potassium hydroxide, dried and distilled. Tetracyclone was prepared according to Johnson and Grummitt⁸ and melted at 219–220°.

Esters of Chloromaleic Acid.—The three esters were prepared in similar fashion. The following description for the di-*n*-propyl ester is representative.

A mixture of 62 g. (0.50 mole) chloromaleic anhydride, 67 g. (1.1 mole) *n*-propanol, and 0.5 g. *p*-toluenesulfonic acid monohydrate was refluxed for 3.5 hours. The solution was diluted with 150 ml. of ether, extracted with cold saturated sodium bicarbonate solution until neutral, dried over anhydrous magnesium sulfate and filtered. After distilling the ether and discarding a small forerun (7.3 g., b. p. 80–89° (1 mm.)), the major product (77 g., 0.33 mole) distilled at 89–90° (1 mm.).

The esters are unsaturated with respect to potassium permanganate in acetone. They are soluble in absolute ethanol, acetone, methyl ethyl ketone, dioxane, ethyl ether, chloroform, carbon tetrachloride, benzene, toluene, petroleum ether (b. p. 60–70°), and acetic acid. They show limited solubility in ethylene glycol, and formic acid (87%) and are insoluble in water.

Esters of Tetraphenylphthalic Acid.—A 1 × 6 in. Pyrex side-arm test-tube was fitted with a condenser to which was attached by means of 5-mm. glass tubing a series of vials. Starting at the condenser these were (1) an empty vial serving as a trap, (2) a vial containing a 1–2 ml. 0.1 *N* silver nitrate solution, (3) another trap, and (4) a vial containing 1–2 ml. of 0.01% solution of palladium(II) chloride solution to test for carbon monoxide. A slow stream of nitrogen was led into the side arm throughout an experiment.

A mixture of 0.38 g. (1.0 mmole) of tetracyclone and 7.0 g. (0.03 mole) of di-*n*-propyl chloromaleate was refluxed over a free flame until the intense purple color of the tetracyclone had changed to brown. During this time the effluent gases turned blue litmus red, the vial holding the silver nitrate solution deposited a curdy white precipitate (silver chloride) and the vial holding palladium(II) chloride solution deposited a black precipitate. The reaction mixture was dissolved in 4 ml. of acetic acid, diluted with water to incipient crystallization and extracted with warm (40–45°) petroleum ether (b. p. 60–70°). Concentration of the petroleum ether gave 0.42 g. (0.76 mmole) of colorless crystals, m. p. 196.5–197.5°, which subsequent recrystallizations did not raise.

The esters are saturated with respect to potassium permanganate in acetone.

When the recrystallization of the *n*-propyl ester was attempted from ethanol, the substance melted over a wide range. Three recrystallizations gave a compound melting at 205–206° (reported^{2,5} 205–206°) which showed no depression in a mixed melting point with authentic di-ethyl tetraphenylphthalate.

Anal. Calcd. for C₂₆H₃₀O₄: C, 82.10; H, 5.74. Found: C, 81.93; H, 5.62.

(8) J. R. Johnson and O. Grummitt, *Org. Syn.*, **23**, 92 (1943).

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POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 2, NEW YORK RECEIVED JUNE 5, 1950

Isotope Exchange Reaction of Chloroform-*d* with Bromoform

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This note reports an infrared spectrophotometric investigation of the deuterium exchange reaction $\text{CCl}_3\text{D} + \text{CBr}_3\text{H} \rightleftharpoons \text{CCl}_2\text{H} + \text{CBr}_3\text{D}$.

The isotope exchange was studied in the liquid phase at 30 and 105°, and in the vapor phase at 105°. The influence of organic bases such as *n*-butylamine and piperidine on the rate of the exchange was observed.

The CCl₃D and CBr₃D were prepared by the reaction of sodium deuteroxide with chloral and bromal, respectively. These products contained as impurities CCl₃H and CBr₃H, to the extent of approximately 10% and 5%, respectively, as determined by infrared and mass spectrometric analysis. The CBr₃H, *n*-butylamine and piperidine were C.P. products which were further purified by fractional distillation under reduced pressure.

The experimental procedure consisted in weighing out small portions (ca. 200 mg.) of the reactants, CCl₃D and CBr₃H, and the desired quantity of base into several ampoules of about 2–4 ml. volume. These were then outgassed several times at –78° and sealed *in vacuo*. After suitable times of reaction in the absence of light at the appropriate temperature the contents were cooled to –78° and held frozen until subsequent analysis. In several experiments no visible decomposition occurred during the course of the reaction. However, in certain cases the solution appeared yellow or dark after an experiment. The volatile contents of the ampoule were then distilled *in vacuo* into another storage ampoule kept at –78°. The residue seldom exceeded 5% (by weight) of the original mixture. In one experiment (15) a special 300-ml. reaction vessel was used; it was large enough to ensure that the reactants as well as the base were completely in the vapor state during the entire reaction. At the conclusion of the experiment, all products were frozen down and analyzed in the usual manner.

The infrared absorption spectra of the mixtures were obtained with a Perkin-Elmer Model 12C spectrophotometer with rocksalt optics, using a 0.027 mm. NaCl cell. The extent of the reaction was determined by measuring the concentration of CBr₃D in the mixtures. The strong doublet at 848 and 864 cm.⁻¹, characteristic of CBr₃D¹ was chosen for the analysis. The extinction coefficient for CBr₃D was obtained using as a calibration standard a 10 mole % solution of CBr₃D in chloroform.

The results reported are based on absorption measurements at 848 cm.⁻¹. In certain of the experiments in the presence of fairly high concentrations of piperidine, interference at 864 cm.⁻¹ due to this molecule was significant. The 864 cm.⁻¹ band was, however, used as a rough check on the analysis, and also served to indicate the extent of decomposition of the piperidine.

The rates of disappearance of CCl₃D and formation of CCl₃H were followed by observing the

(1) S. M. Ferigle, F. F. Cleveland, W. M. Boyer and R. B. Bernstein, *J. Chem. Phys.*, **18**, 1073 (1950).

TABLE I
ISOTOPE EXCHANGE BETWEEN CCl_3D AND CBr_3H
All concentrations expressed as mole fractions.

Expt.	Initial concentrations				Temp., °C.	Time, days	Final CBr_3D	% ex- changed
	CBr_3H	CCl_3D	CCl_3H	Base $(\text{CH}_2)_4\text{NH}$				
1	0.438	0.433	0.048	0.081	105	1.0	0.076	37
2	.422	.470	.052	.056	105	3.6	.079	38
3	.519	.398	.044	.039	105	7.1	.036	17
4	.481	.398	.044	.077	30	0.8	.006	2.9
5	.446	.444	.049	.061	30	3.7	.009	4.4
6	.483	.322	.036	.159	30	13.0	.086	46
7	.417	.489	.054	.040	30	13.0	.038	18
8	.443	.446	.050	0.061	105	0.95	.054	26
9	.424	.429	.048	.098	30	0.9	.011	5.4
10	.464	.401	.045	.090	30	1.1	.028	14
11	.475	.377	.042	.105	30	70	.096	48
12	.418	.401	.045	.135	30	72	.109	56
13	.507	.444	.049		105	7.0	<0.001	<0.1
14	.402	.538	.060		30	4.0	<0.001	<0.1
15	.485	.402	.045	0.068 (Vapor phase)	105	9.0	<0.001	<0.1

change in absorption of the bands at 909 and 760 cm^{-1} , respectively. A precise analysis was not possible for either of these components. Qualitatively, however, these observations were in agreement with the more reliable CBr_3D determinations.

The results are summarized in Table I. Indicated are the initial concentrations of reactants, the reaction conditions and the final concentration of CBr_3D . The "% exchange" is defined in terms of the expected equilibrium concentration of CBr_3D , on the basis of an equilibrium constant of unity for the isotope exchange reaction. An approximate calculation² of the equilibrium constant K for this reaction was carried out on the basis of the most recent frequency assignments for each of the two isotopic pairs.³ At 30° the equilibrium constant for the exchange was calculated to be 0.90 ± 0.03 . The rather large uncertainty in this value is due in part to the uncertainty in the important ν_4 degenerate frequency for CBr_3D , which is not directly observed because of Fermi resonance interaction with a combination tone. Fortunately, under the conditions of the exchange experiments, the error in the "% exchanged" resulting from the use of a value of $K = 1.0$ is small.

Because of the difficulty in preparing a series of solutions with constant mole fraction of base, it is not possible to compare directly the results of otherwise comparable experiments where there is an appreciable difference in base concentration.

The large discrepancies in the experimental

(2) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261-267 (1947).

(3) CBr_3D : Ferigle, *et al.*, ref. (1); CBr_3H : A. G. Meister, S. E. Rosser and F. F. Cleveland, *J. Chem. Phys.*, **18**, 346 (1950); CCl_3D : J. R. Madigan, F. F. Cleveland, W. M. Boyer and R. B. Bernstein, *ibid.*, **18**, 1081 (1950); CCl_3H : J. P. Zietlow, F. F. Cleveland, A. G. Meister, *ibid.*, **18**, 1076 (1950).

results are due in part to the differences in initial base concentrations. Another contributing factor is the progressive decomposition occurring during the course of the reaction. In two additional experiments with 1.0 mole % butylamine, less than 0.1% exchange occurred in eight days at 30 and 105°, respectively. This suggests that the minimum initial percentage of base required to catalyze the exchange is greater than 1%.

A quantitative kinetic treatment of the experimental results does not appear possible in view of these considerations. However, certain deductions of a qualitative nature may be drawn from the data.

Experiments 13 and 14 at 105 and 30° show that the rate of the exchange of CCl_3D with CBr_3H is extremely slow for the pure compounds alone. In the presence of *n*-butylamine or piperidine (in excess of *ca.* 4 mole %) the liquid phase exchange proceeds at a measurable rate (experiments 1-12). On the other hand, the results of experiment 15 indicate that the exchange is negligibly slow in the vapor state and that the organic base has no catalytic effect when all components are in the gas phase. After nine days, less than 0.1% exchange had taken place.

These results appear to lend support to an ionic mechanism for the exchange. Detailed kinetic studies of the dependence of the isotope exchange rate on the concentration and basic strength of amine are necessary in order to clarify the mechanism further.

Acknowledgments.—The authors are indebted to Profs. M. Kilpatrick and S. Siegel for helpful discussions. Thanks are also due to Dr. V. H. Dibeler, Dr. Sidney Katz, Mr. W. M. Boyer and Mr. D. V. Kniebes. The D_2O was obtained from the Atomic Energy Commission.