dine had been oxidized to iodate, by the method of Evans, *et al.*[2] From the reactor the reaction products were pumped through a Dry Ice trap and 4 liquid nitrogen traps where the condensable products were collected for analysis by mass spectrometer. Helium and non-condensable gases were removed by a vacuum pump controlled by a manometer to produce the desired pressure in the range of 6.2 to 8.7 mm. Flow rates of helium and methyl bromide were controlled by very small jets operating at sonic velocity. Prior to an experiment the system was evacuated with diffusion pumps to less than 10^{-5} mm.

Materials.—Helium was obtained from the Mathieson Chemical Company and was stated to be of 99.9% purity. Any traces of oxygen present were removed by adsorption on activated carbon at liquid nitrogen temperatures. The methyl bromide, obtained from the Mathieson Company was used directly. Its purity was stated to be 99.4%. The isopropyl iodide used was a mid boiling point fraction (89.2°) from a distillation of "Eastman Grade" isopropyl iodide.

In the initial experiments, iodine was introduced into the reactor section to determine the relative concentration of methyl radicals available for reaction. (Zero activation energy was assumed for the reaction between methyl radicals and molecular iodine.) The resulting methyl iodide was determined by mass spectrometric analyses of the condensed product. The first two columns in the table summarize the calibration runs. In the remainder of the experiments the reactor was loosely packed with silver gauze and isopropyl iodide was brought into the reactor in place of iodine.

	Calibration		Displacement study			
Reactor temp., °C.	304	304	304	304	327	326
Helium circulated:						
Total, moles/sec. × 10^4	3.12	3.25	3.28	3.32	3.40	3.23
Over sodium, moles/sec. × 10^4	0.49	0.49	0.49	0.49	0.49	0.49
Partial pressures, mm.:						
Methyl bromide	.08	.09	.09	.06	.06	.05
Sodium	.03	.06	.03	.03	.03	.03
Iodine	.02	.03	0	0	0	0
Isopropyl iodide	0	0	0.04	0.17	0.36	0.22
Mmoles charged:						
Methyl bromine	28.2	24.1	52.9	34.9	19.2	23.2
Sodium	12.4	19.6	14.9	14.5	9.1	11.2
Iodine	6.6	6.9	0	0	0	0
Isopropyl iodide	0	0	31.7	121.3	141.7	128.0
Yield of methyl radicals:						
Mmoles to reactor	0.17	0.18	0.36[a]	0.36[a]	0.20[a]	0.29[a]
Mole % of sodium charge	2.5	2.6	....	....	.....	....
Methyl iodide recovered, mmoles	0.17	0.18	0.06	Trace	0.02	....
Mmoles I deposited on silver wire	.....	...	0.0047	0.0055	0.0063	0.0079
% Displacement (after corrn. for thermal dec.)	.....	...	1.3	1.5	0.05	0.81
Duration of exp., sec.	10,800	9000	17,800	18,000	9900	14,400

[a] Based on first two calibration runs.

In the displacement study the amount of iodine deposited on the silver gauze was considered to be a measure of the displacement reaction after correction for thermal effects based on "blank runs" with isopropyl iodide in the presence of the silver gauze. At 304° the thermal decomposition of the iodide was negligible, but at 327° the decomposition proceeded to an extent equivalent to 1.4% of the methyl radicals reaching the reactor section. At much higher temperatures (385°) the formation of iodine was 16-fold that predicted from the velocity constants of Butler, Mandell and Polanyi[3]; thus, the silver gauze appeared quite effective for the detection of iodine in the system. The rate constants reported in the preceding reference were determined over an interval of 400–490° and result in an unreasonably low activational energy, which the authors attribute to recombination at the higher temperatures. However, this factor should not greatly affect the present comparison.

On the basis of the simple collision theory, it is estimated that the methyl concentrations and reaction times employed were sufficient for the detection of the displacement reaction only if the corresponding activational energy does not exceed 10 to 15 kcal. From the very meager indications of displacements (0.05–1.5% of the methyl radicals entering the reactor) it is concluded only that appreciable displacement does not occur in the homogeneous phase or on the silver surface at these temperatures. Small amounts of methyl iodide were found in the products of reaction which might have been formed by the reaction of methyl radicals and iodine atoms or by extraction from the isopropyl iodide. With the primary methyl radical it appears that the expected extraction (of hydrogen and perhaps iodine) reactions predominated over the displacement of iodine.

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REFINING TECHNICAL AND RESEARCH DIVISIONS
HUMBLE OIL & REFINING COMPANY
BAYTOWN, TEXAS

Perfluorinated Alkene, Alkyne and Cycloalkene

BY ALBERT L. HENNE AND KAZI ABDUL LATIF

RECEIVED JUNE 29, 1953

The synthesis of perfluoro-2-butene, CF_3-$CF{=}CFCF_3$ and of perfluorocyclopentene,

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[2] R. M. Evans, W. F. Hanson, Jr., and P. K. Glasoe, *Ind. Eng. Chem., Anal. Ed.*, **14**, 314 (1942).

[3] E. T. Butler, Erna Mandell and M. Polanyi, *Trans. Faraday Soc.*, **41**, 298 (1945).

$\overline{CF{=}CFCF_2CF_2CF_2}$ has been performed in preparation for a study[1] of their behavior toward anionic reagents in contrast to $CF_3CCl{=}CClCF_3$ and $\overline{CCl{=}CClCF_2CF_2CF_2}$. The 2-butene, which we prepared previously,[2] can now be claimed as the *cis*-isomer by comparing our data with those just published by Brice and his co-workers.[3] The cyclopentene is new; in one of its attempted syntheses, a new perfluoroalkyne $CF_3C{\equiv}C{-}CF_2CF_3$ was obtained instead of the cyclic compound.

When Newby[2] first reported his synthesis of $CF_3CF{=}CFCF_3$ by dechlorination of $CF_3CFClCFClCF_3$, he gave a boiling range of +0.4 to 3.0° at 760 mm. Park[4] obtained a sample boiling about −4.5° by pyrolysis of Teflon. Miller[5] reported a b.p. of 1.2° for a sample prepared in a way similar to Newby's. No one made any claim to a particular geometric isomer. The sample prepared by Brice[3] by pyrolysis of $C_4F_9CO_2K$ was, however, reported as boiling at 0° and was considered substantially a 50–50 mixture of *cis*- and *trans*-isomers on the basis of an infrared analysis.

The C_4F_8 synthesis[2] was repeated by quantitatively dechlorinating $CF_3CFClCFClCF_3$ (obtained from $CF_3CCl{=}CClCF_3$ and nascent HgF_2) with zinc in boiling ethanol and collecting C_4F_8 as evolved, in 24 hours. An Engler distillation, with thermometer immersed in the liquid gave a boiling range of +0.2 to +1.5° at 743 mm. We are thus confirming our former observation and that of Miller, on samples similarly prepared; this boiling point is appreciably higher than the values obtained on the samples prepared by pyrolysis. Our sample showed a strong absorption band[6] (84% absorption) about 5.8 μ; this is the band (5.77) which Brice reported as *weak* in his original sample, and *reinforced* when the higher boiling reaction of his sample was enriched. As stated hereunder this band was also found at about 5.7 μ in the new cyclo-C_5F_8, a compound which has, of necessity, the *cis*-configuration. We conclude therefore that samples prepared by the sequence $CF_3CCl{=}CClCF_3$ to $CF_3CFCl{-}CFClCF_3$ to $CF_3{-}CF{=}CF{-}CF_3$ are predominantly the *cis*-isomer; Brice's sample obtained by pyrolysis of perfluorovaleric acid is said by him to be a mixture of *cis–trans* isomers; and we suggest that the low boiling sample obtained by Park in the pyrolysis of Teflon might have been rich in the *trans*-isomer.

Of the perfluorinated cyclic olefins, cyclo-C_4F_6 has been reported from here[7] and cyclo-C_6H_{10} has been described by Brice and Simons.[8] A perfluorinated cyclopentene p.b. 33–35° is mentioned by Park and co-workers[9] as one of the pyrolysis products of $CHClF_2$, with formula suggested from general analogy.

To prepare cyclo-C_5F_8, a $\overline{CCl{=}CCl{-}CF_2{-}CF_2{-}CF_2}$ sample was sent to Dr. George Cady, at the University of Washington, who subjected it to the action of CoF_3 at a temperature of 90° (initial) to 200° (final) in a stream of nitrogen. There was no evidence of chlorine in the effluent gases and addition of fluorine was thus found to proceed quantitatively, without substitution or significant decomposition. The product boiled at 84–85° and froze as a mush slightly below room temperature. Separation of the product (b.p. 85°) from any remaining original material (b.p. 88°) was not practical, so the crude cyclo-$C_5F_8Cl_2$ was dechlorinated with zinc in boiling ethanol and the cyclo-C_5F_8 collected as it was evolved, over a period of 24 hours. Cyclo-C_5F_8 was found to boil at 25.4 to 26.5° under 743 mm. by Engler distillation with immersed thermometer. Its analysis showed 69.6% F, theory 71.6%. The infrared spectrum showed a strong absorption (92%) band at 5.7 μ attributed to C=C stretching, and the customary C–F stretching bands at 7 μ to 9 μ. The geometrical configuration is, of necessity, *cis*. As the difficult fluorine analysis of cyclo-C_5F_8 was not as close as desired, chlorine was added back to the cyclo-olefin. The addition was very sluggish, as it always is with cyclic fluorides; it gave cyclo-$C_5F_8Cl_2$, b.p. 83.0 to 83.5° at 740 mm., n^{20}_{D} 1.3335, $d^{28.5}_4$ 1.7235, M_{R} 33.6, AR_{F} 1.19, % Cl 24.4, calcd. 25.0, no absorption up to 7 μ (C–F bands only).

In attempts to prepare cyclo-C_5F_8 by carrying the conventional fluorination of cyclo-C_5Cl_8 past the $\overline{CCl{=}CCl{-}CF_2{-}CF_2{-}CF_2}$ stage, it was observed that the use of SbF_3Cl_2 instead of SbF_3 as fluorinating agent would cause the formation of varied quantities of a material boiling about five degrees below the main cyclo-$C_5F_6Cl_2$ (88°) fraction. This material, b.p. 80–88°, n^{20}_{D} 1.3443 to 1.3532, was accumulated and on conventional treatment with zinc in boiling alcohol, it gave off a gaseous material (about 27% yield) and left cyclo-$C_5F_6Cl_2$ behind; the raw material was thus a mixture. This gaseous material, b.p. 7.5°, was first believed to be cyclo-C_5F_8, as its molecular weight was determined as 220 by gas density (theory 212); however, it was found to accept one mole of chlorine with unexpected facility, to yield $C_5F_8Cl_2$, b.p. 84.5 to 85.5° under 740 mm., n^{24}_{D} 1.3401, d^{24}_4 1.6682, M_{R} 35.55, AR_{F} 1.22, proposed formula $CF_3CCl{=}CClCF_2CF_3$, 25.17% Cl found, 25.08 calcd. Then it was found that, with intense illumination, a second mole of chlorine could be forced on, to yield $C_5F_8Cl_4$, b.p. 145–147° under 748 mm., n^{24}_{D} 1.3838, $d^{28.5}_4$ 1.8238, M_{R} 45.2, AR_{F} 1.15, proposed formula $CF_3CCl_2CCl_2CF_2CF_3$, 40.2% Cl found, 40.1% calcd. Evidently the compound had an open chain with either one triple bond or else two double bonds.

This alternative was solved by oxidation with alkaline permanganate[10] of the dichloro compound presumed to be $CF_3CCl{=}CClCF_2CF_3$. The oxidation gave an acid fraction, b.p. 95–108°, n^{20}_{D} 1.3205–1.3130, the index of which went down as the distillation temperature rose. This was esterified with ethanol, and the ester (dried on P_2O_5) distilled in the 51 to 73° range. The 73° fraction was treated with ammonia to give $C_2F_5CONH_2$, m.p. 93°, no depression in mixed m.p., while the 51° fraction gave CF_3CONH_2, m.p. 71° (mixed m.p. 73–73.5 with an authentic sample 74°). Since perfluoroacetic and propionic acids were the only oxidation products, the formula of the C_5F_8, b.p. 7.5°, must be $CF_3{-}C{\equiv}C{-}CF_2CF_3$. In agreement, infrared examination showed a weak (28% absorption) band at 4.9 μ, attributed to the $-C{\equiv}C-$.

Had the original C_5F_8 been a diene, $CF_2{=}CF{\cdot}CF{=}CF{\cdot}CF_3$ or $CF_2{=}CF{\cdot}CF_2{\cdot}CF{=}CF_2$, the respective dichlorides, $CF_2Cl{-}CF{=}CF{-}CFClCF_3$ or $CF_2Cl{-}CFCl{\cdot}CF_2{\cdot}CF{=}CF_2$ would have given chlorine-containing acids, which were searched for, and not found.

Addition in Press.—When the fluorine addition to cyclo-$C_5F_6Cl_2$ was repeated by Dr. Tatlow at the University of

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[1] Kazi Abdul Latif, Ph.D. dissertation, The Ohio State University (1952), *J. Indian Chem. Soc.*, first part in press.

[2] A. L. Henne and T. H. Newby, THIS JOURNAL, **70**, 130 (1948), and T. H. Newby, Ph.D. dissertation, The Ohio State University (1945).

[3] T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearlson, *ibid.*, **75**, 2698 (1953).

[4] J. D. Park, private communication.

[5] W. T. Miller, in Slesser and Schram, "Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds," McGraw–Hill Book Co., Inc., New York, N. Y., Chapt. 32, p. 677.

[6] Infrared spectrograms were taken with a Baird Associates instrument using a NaCl prism and a 5-cm. cell: all samples were gases at 300 mm.

[7] A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

[8] T. J. Brice and J. H. Simons, *ibid.*, **73**, 4017 (1951).

[9] J. D. Park and others, *Ind. Eng. Chem.*, **39**, 354 (1947).

[10] A. L. Henne, T. Alderson and M. S. Newman, THIS JOURNAL, **67**, 918 (1945).

Birmingham, a pure sample of cyclo-$C_5F_8Cl_2$, m.p. 28°, was collected by sublimation. Dechlorination to cyclo-C_5F_8 by Dr. Joan Banus, here, gave a sample on which she observed a vapor pressure $\log p_{\mathrm{mm}} = 7.996 - (1526/T)$ over the range $-36°$ to $+26°$; normal b.p. 25.2°; ΔH at b.p. 6963 cal.; Trouton constant, 23.3; mol. wt., 212.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

Rate of Deuterium Exchange of Certain Amines and Alcohols[1,2]

BY JACK HINE AND CYRUS H. THOMAS

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Deuterium exchange involving atoms without unshared electron pairs has often been found to proceed slowly enough for study by ordinary kinetic methods. In addition to numerous cases involving carbon atoms, the exchange of cobalt, platinum and palladium ammines has been found to proceed at a measurable rate,[3] and although the ammonium ion has been found to exchange rapidly with liquid ammonia[4] its rate of exchange with acidic aqueous solutions may be measured.[5] The situation with regard to the ease of exchange of hydrogen bound to halogen, oxygen, sulfur, trivalent nitrogen, etc., is less clear, however.

There have been two reports of measurable rates of exchange between hydrogen sulfide and alcohols at temperatures of $-80°$ and below.[6] On the other hand, ionization equilibria for ordinary acids and bases in aqueous solution usually appear to be established rapidly[7] and, contrary to an earlier report,[8] alcohols do not exchange with water slowly.[9] However, since only a few cases have been studied in this regard, we have felt it worthwhile to investigate certain additional examples.

Since the rate of exchange might well depend on the acidity and basicity of the reactants and since ammonia appears to be less than $1/10^{19}$ as strong as an acid as water[10] while less than 10^{11} times stronger as a base,[11] it seemed reasonable to study the deuterium exchange between two amines.[12] In the exchange between ethylamine and *n*-heptylamine, however, equilibrium was found to be established too rapidly to measure. In hope that the exchange might be susceptible to steric hindrance, we have studied the exchange between *t*-butyl alcohol and di-*t*-butylisopropylcarbinol, but have found it too fast to measure also. The exchange between ethylamine and *t*-amyl alcohol also was found to be rapid. Since it appears that the kinetics of reactions of this type may be studied, at best, only by methods capable of measuring very rapid reactions or by use of compounds differing in some fundamental way from ours, we have discontinued our investigation.

Experimental

Reagents.—The ethylamine, *t*-butyl alcohol and *t*-amyl alcohol were commercial materials, suitably dried and fractionated. Deuterium oxide (99.8%) was obtained from the D. A. Stuart Oxygen Company on allocation from the Atomic Energy Commission. The *n*-heptylamine was prepared by the method of reference 13 and the di-*t*-butylisopropylcarbinol (n^{25}_{D} 1.4592) by that of Bartlett and Schneider.[14] Deuterated ethylamine and *t*-butyl alcohol were prepared by equilibration with deuterium oxide, fractional distillation, drying and redistillation.

Exchange Reactions.—The deuterated ethylamine used was found to differ from its pure protium analog by absorbing much more weakly at 2.9 μ. Accordingly, a weighed amount (about 1 ml.) of deuterated ethylamine in a sealed glass tube was placed in a flask containing *n*-heptylamine at $-11°$. The flask was shaken (breaking the sealed tube) for a few seconds until all of the schlieren had disappeared and then the ethylamine was immediately removed under vacuum. The absorption at 2.9 μ for the material collected had already increased to the same equilibrium value found when the reaction was allowed to proceed for several hours. Exchange of ethylamine and *t*-amyl alcohol was similarly found to be rapid. By measurement at 3.86 μ, where deutero-*t*-butyl alcohol absorbs much more strongly than its protium analog, the exchange between di-*t*-butylisopropylcarbinol and *t*-butyl alcohol was found to occur too rapidly to measure at the melting point of *t*-butyl alcohol (25°).

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[1] This study was carried out as part of a project sponsored by the Atomic Energy Commission.

[2] From a Ph.D. thesis submitted by Cyrus H. Thomas to the Graduate School of the Georgia Institute of Technology.

[3] See J. S. Anderson, H. V. A. Briscoe, L. H. Cobb and N. L. Spoor, *J. Chem. Soc.*, 367 (1943), and earlier references given therein.

[4] C. J. Nyman, S. C. Fung and H. W. Dodgen, THIS JOURNAL, **72**, 1033 (1950).

[5] A. I. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S. S. S. R.*, **74**, 513 (1950); *C. A.*, **45**, 424a (1951). This also has been found to be the case by Dr. C. G. Swain who is studying reactions of this type in considerably more detail (private communication).

[6] K. H. Geib, *Z. Elektrochem.*, **45**, 648 (1939); A. Tananger, *Tids. Kjemi, Bergvesen, Met.*, **3**, 44 (1943); *C. A.*, **39**, 2438^4 (1945).

[7] However, see A. G. Ogston, *J. Chem. Soc.*, 1023 (1936).

[8] W. J. C. Orr, *Trans. Faraday Soc.*, **32**, 1033 (1936).

[9] J. C. Jungers and K. F. Bonhoeffer, *Z. physik. Chem.*, **A177**, 460 (1936); J. Hine and C. H. Thomas, THIS JOURNAL, **75**, 739 (1953).

[10] Potassium amide metallates diphenylmethane [C. B. Wooster and N. W. Mitchell, *ibid.*, **52**, 688 (1930)] which has been assigned a "*pK*" value of at least 35 [W. K. McEwen, *ibid.*, **58**, 1124 (1936)].

[11] From their respective ionization constants in methanol, I. M. Kolthoff and L. S. Guss, *ibid.*, **60**, 2516 (1938), and H. Goldschmidt and P. Dahll, *Z. physik. Chem.*, **108**, 121 (1924).

[12] Since the completion of this work it has come to our attention that the exchange between deutero-ammonia and hydrazine also has been found to be quite rapid [P. C. Cross and P. A. Leighton, THIS JOURNAL, **60**, 981 (1938)].

[13] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 318.

[14] P. D. Bartlett and A. Schneider, THIS JOURNAL, **67**, 141 (1945).

SCHOOL OF CHEMISTRY
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

The Separation of Adjacent Rare Earths with Ethylenediamine-tetraacetic Acid by Elution from an Ion-exchange Resin[1]

BY F. H. SPEDDING, J. E. POWELL AND E. J. WHEELWRIGHT

RECEIVED JULY 15, 1953

Two general types of rare earth separations involving ion exchange have been described in publications from this Laboratory—the citrate elution[2] and the ethylenediaminetetraacetic acid (E.D.T.-A.) fractionation.[3] The two methods make use of quite different principles. The citrate separation involves the adsorption of a band of rare earth ions on an ion-exchange resin bed and the subsequent elution of the band down the column. The separation which occurs is a result of the individual rare

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, THIS JOURNAL, **72**, 2354 (1950); F. H. Spedding, E. I. Fulmer, J. E. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951); also see earlier papers.

[3] E. J. Wheelwright and F. H. Spedding, *ibid.*, **75**, 2529 (1953).