Birmingham, a pure sample of cyclo-$C_6F_8Cl_2$, m.p. 28°, was collected by sublimation. Dechlorination to cyclo-C_6F_8 by Dr. Joan Banus, here, gave a sample on which she observed a vapor pressure $\log p_{mm} = 7.996 - (1526/T)$ over the range −36° to +26°; normal b.p. 25.2°; ΔH at b.p. 6963 cal.; Trouton constant, 23.3; mol. wt., 212.

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

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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).

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

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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).

earth bands coming to equilibrium with the eluate. The concentrations of the various ions in the eluate automatically adjust themselves, as determined by the stability constants of the various rare earth–citrate complexes,[4] and therefore one band succeeds another as they come off the column.

In the second method, enough E.D.T.A. is added to complex only part of the rare earth mixture. The E.D.T.A. complexes more strongly with the rare earths whose E.D.T.A stability constants are greater. This mixture is passed through an ion-exchange bed which is in the ammonium cycle, the exchanger acting only as a filter. The heavier rare earths which are more strongly complexed pass through the column, while the uncomplexed ions, mostly lighter rare earths, adsorb on the resin. With a single operation this method allows the separation of a complex rare earth mixture into fractions which contain only a few adjacent rare earths.

The stability constants of the rare earth-E.D.T.-A. complexes have been measured,[5] and they vary from $10^{14.72}$ for lanthanum to $10^{19.65}$ for lutetium. The difference corresponds to a factor of $10^{4.9}$ or as a mean of 2.38 from one rare earth to the next. The rare earth–citrate complexes have not been measured, but since E.D.T.A. is a hexadentate chelating agent while the two citrate anions associated with the rare earths are tridentate complexing agents, the E.D.T.A.-rare earth constants should be much more sensitive to ion size, and the differences between them should be larger than the differences between those of the rare earth–citrate complexes.

It would be very desirable, in light of the larger differences between the constants, if E.D.T.A. could be used as an elution agent. It has the advantage that a more concentrated solution can be used, but it has the disadvantage that E.D.T.A. precipitates in acid media; hence, no part of the resin bed through which the E.D.T.A. passes can be in the acid cycle. Several investigators have attempted to elute rare earths with E.D.T.A., for example, A. E. Taylor of the University of Illinois,[6] but evidently did not find the proper conditions for successfully separating the rare earths by this means.

Since the rare earth ions complex very strongly with E.D.T.A. under almost all normal operating conditions for column elution, the complexed ions tend to pass directly through ion exchange beds which contain cations whose E.D.T.A. stability constants are smaller than those of the rare earths. We have been able to overcome this difficulty by eluting the rare earth ions down an ion-exchange column in the iron cycle. The stability constant of the E.D.T.A.–iron(III) complex has been found[7] to be 10^{25}, much larger than any of the rare earth constants; consequently, during the elution process, when the rare earth complex reaches the iron phase resin, an exchange takes place and the rare earth is readsorbed. Since iron complex is soluble, it is swept out the bottom of the column. The various rare earth bands evidently operate in the same manner. As a less tightly held rare earth complex comes in contact with a rare earth ion which forms a more stable complex, an exchange takes place. Gradually, with repeated exchanges, the concentrations of the heavier rare earths increase and approach 100% in the individual leading bands, while the concentrations of the lighter rare earths increase and approach 100% in the individual trailing bands. There is always a small region of mixed rare earths between any pair of bands. The width of this region depends upon such factors as flow rate, resin particle size, etc.

Preliminary runs have indicated that this method is very efficient in separating adjacent rare earths. While the conditions described below are by no means optimum, it was felt that the results should be reported at this time since they indicate that larger quantities of rare earths can be processed through smaller ion-exchange columns in a much shorter period of time than by previous methods. Whether the degree of purity of the individual rare earths which are attained with the citrate elution can also be achieved in the E.D.T.A. elution remains to be seen.

Experimental

A rare earth chloride solution was prepared by dissolving equal amounts of Pr_6O_{11} and Nd_2O_3 in a slight excess of HCl. The *p*H of the solution was adjusted to 5 with the addition of NH_4OH, and the solution was passed through a small column containing Nalcite HCR. The amount of solution was sufficient to completely saturate the resin with rare earths. The amount of rare earth which was adsorbed on the resin was determined by the difference between that originally dissolved and that which passed through the column. A second column of similar size, but containing 30% more resin, was saturated with iron(III) by passing a solution of $Fe(NO_3)_3$ through it. This was followed by water to remove the ammonium and nitrate ions. The bottom of the first column was then connected to the top of the second, and the system was eluted with a solution containing 10 g. of the diammonium dihydrogen salt of E.D.-T.A. per liter and adjusted to a *p*H of 8.04 with NH_4OH. The flow rate was fixed at 50 ml. per hour and the eluate was collected in 200-ml. fractions, the rare earth content of each being precipitated with oxalic acid, filtered, washed and ignited to the oxide. These individual samples were then redissolved and analyzed spectrophotometrically for individual rare earth content. Table I shows the analyses of the nine fractions obtained.

TABLE I

RARE EARTH OXIDES RECOVERED IN ONE RUN ON Nd–Pr MIXTURE (GRAMS)

Sample no.	Nd_2O_3	Pr_6O_{11}	Sample no.	Nd_2O_3	Pr_6O_{11}
1	0.1200	....	6	0.0279	0.8178
2	.6710	....	7	....	.8434
3	.8513	0.0133	8	....	.8174
4	.7899	.0493	9	....	.0108
5	.3946	.4446	Total	2.8547	2.9966

The above experiment indicated that a rapid method for separating individual rare earths with E.D.T.A. is possible. This investigation is being continued.

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(4) F. H. Spedding and J. E. Powell, unpublished.

(5) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, THIS JOURNAL, **75**, 4196 (1953).

(6) A. E. Taylor, United States Atomic Energy Commission, Report NP-1434.

(7) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).