

Birmingham, a pure sample of cyclo-C<sub>6</sub>F<sub>8</sub>Cl<sub>2</sub>, m.p. 28°, was collected by sublimation. Dechlorination to cyclo-C<sub>6</sub>F<sub>8</sub> by Dr. Joan Banus, here, gave a sample on which she observed a vapor pressure  $\log p_{\text{mm}} = 7.996 - (1526/T)$  over the range -36° to +26°; normal b.p. 25.2°;  $\Delta H$  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<sup>1,2</sup>

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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 amines has been found to proceed at a measurable rate,<sup>3</sup> and although the ammonium ion has been found to exchange rapidly with liquid ammonia<sup>4</sup> its rate of exchange with acidic aqueous solutions may be measured.<sup>5</sup> 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.<sup>6</sup> On the other hand, ionization equilibria for ordinary acids and bases in aqueous solution usually appear to be established rapidly<sup>7</sup> and, contrary to an earlier report,<sup>8</sup> alcohols do not exchange with water slowly.<sup>9</sup> 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<sup>19</sup> as strong as an acid as water<sup>10</sup> while less than 10<sup>11</sup> times stronger as a base,<sup>11</sup> it seemed reasonable to study the deuterium exchange between two amines.<sup>12</sup> 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*<sup>2</sup>D 1.4592) by that of Bartlett and Schneider.<sup>14</sup> 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  $\mu$ . 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  $\mu$  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  $\mu$ , where deuterio-*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°).

(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<sup>1</sup>

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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<sup>2</sup> and the ethylenediaminetetraacetic acid (E.D.T.-A.) fractionation.<sup>3</sup> 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

(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).

(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. 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. Kjem. Bergvesen, Met.*, **3**, 44 (1943); *C. A.*, **39**, 2438<sup>a</sup> (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 deuterio-ammonia and hydrazine also has been found to be quite rapid [P. C. Cross and P. A. Leighton, *THIS JOURNAL*, **60**, 981 (1938)].