

absorption spectrum together with that of the two thioctic acids and *n*-propyl disulfide is shown in Figure 1. A light-induced fading of diphenylpicrylhydrazyl<sup>22</sup> at room temperature and dependent upon the presence of the disulfide was demonstrated. A photochemical polymerization of the disulfide by light of wave length greater than 4,000 Å. was sensitized by Zn tetraphenylporphin. These results may be taken to indicate that the dissociation energy of the disulfide bond in this compound is something less than 50 kcal. and that this dissociation may be brought about by energy transfer from some other molecule in a suitably excited state.

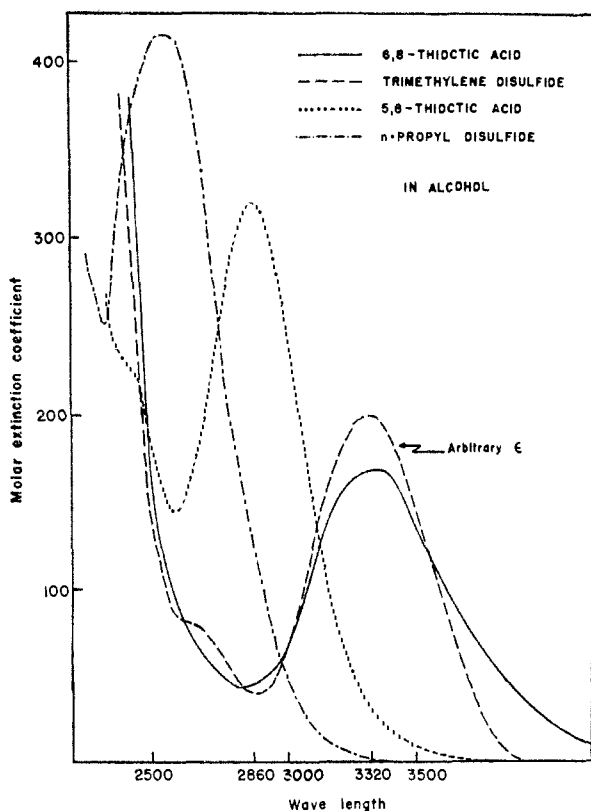


Fig. 1.—Absorption spectra of several disulfides.<sup>23</sup>

That such energy transfers may take place, and especially efficiently in condensed systems, has been amply demonstrated.<sup>23,24,25,26,27</sup> Since the grana have the optical properties of a condensed chlorophyll phase,<sup>28,29,30,31</sup> a quantum absorbed anywhere within that phase is very rapidly transferred among the identical molecules of that phase at the singlet or the triplet levels. Concomitant with this, there occurs a decrease in the prob-

(22) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1217 (1951).

(23) H. Kallman and M. Furst, *Phys. Rev.*, **79**, 857 (1950).

(24) H. Kallman and M. Furst, *ibid.*, **81**, 853 (1951).

(25) H. Kallman and M. Furst, *ibid.*, **85**, 816 (1952).

(26) M. M. Moodie and C. Reid, *J. Chem. Phys.*, **20**, 1510 (1952).

(27) C. Reid, *Phys. Rev.*, **88**, 422 (1952).

(28) S. Granick and K. R. Porter, *Am. J. Bot.*, **34**, 545 (1947).

(29) M. Calvin and V. Lynch, *Nature*, **169**, 455 (1952).

(30) E. E. Jacobs and A. S. Holt, *J. Chem. Phys.*, **20**, 1326 (1952).

(31) A. Frey-Wyssling and K. Mühlethaler, *Vierteljahrsschrift der Naturf. Ges. Zurich*, **94**, 182 (1949).

ability of emission as fluorescence<sup>23,24,25,32</sup> and hence an increase in the availability of the quantum for chemical transformation (disulfide fission). In such a system, the high efficiency of energy conversion may be retained even though the ratio of chlorophyll to disulfide molecules be large ( $10^2$ – $10^3$ ).

(32) D. McClure, private communication.

(33) We are indebted to Mr. Paul Hayes for the determination of these absorption spectra.

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### ELECTROCHROMATOGRAPHIC SEPARATIONS OF RARE EARTHS

Sir:

Differential electrical migration in moist filter paper,<sup>1,2,3</sup> which has provided continuous<sup>3</sup> and discontinuous<sup>2</sup> separations of many ions, has now been applied to the separation of rare earths. These applications have incorporated many of the desirable physical and sorptive features of paper chromatography, and they have also utilized the principles of complex formation previously employed for the ion-exchange chromatography of rare earths.<sup>4</sup> They have yielded the resolved ions in a readily detectable and recoverable form.

For one-way, discontinuous migrations, filter paper (Eaton-Dikeman, Grade 301, 0.03 inch thick)<sup>1</sup> 3 to 6 feet by 20 inches was moistened with the electrolytic solution. About 50  $\mu$ l. of the radioactive mixtures (about 0.3  $\mu$ c. per component) and separate reference solutions of the components were added near the center.<sup>1</sup> The paper was encased in a polyethylene sheet, and the ends were dipped into separate portions of the electrolytic solution (8 l.) After electrolysis (5 v. per cm.,

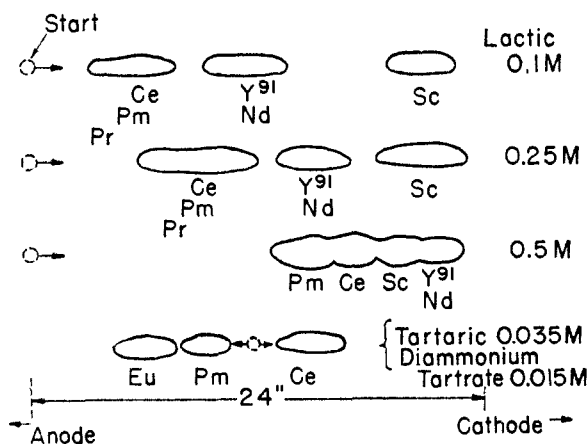


Fig. 1.—Migration of rare earths in lactic acid (24 hr.) and in tartrate solution (48 hr.).

(1) H. H. Strain, *Anal. Chem.*, **24**, 356 (1952).

(2) H. H. Strain and G. W. Murphy, *ibid.*, **24**, 50 (1952).

(3) T. R. Sato, W. P. Norris and H. H. Strain, *ibid.*, **24**, 776 (1952).

(4) Ion Exchange, Plutonium Project Reports, THIS JOURNAL, **69**, 2769–2881 (1947).

1 to 2 days),<sup>5</sup> the paper was dried, and the ions were located photographically.<sup>3</sup>

As indicated in Fig. 1, the separability of rare earths increased with decreasing concentration of the supporting electrolyte, lactic acid. Although the mobility was great in about 1.5 *M* acid, Sc trailed the unseparated rare earths. In acid less than 0.1 *M*, electromigration produced slowly migrating, elongated zones. This migration behavior and the separability of the zones depended upon the selective sorbability of the ions by the paper. Separate chromatographic experiments showed that the sorbability of the ions increased with decreasing concentration of the lactic acid as has been found with Ca.<sup>5</sup>

In 0.1 *M* lactic acid, the rate of separation of Y from Ce increased during the electrolysis. Various cations separated in the following sequence (decreasing mobility): Cs + Rb, Sr, Ca, Co, Zn, Cu, Sc, Y<sup>90</sup> + Y<sup>91</sup> + Nd, Ce + Pr + Pm + Eu, Hg + Zr + Nb. The Hg + Zr + Nb did not migrate, but if stabilized with oxalate Zr + Nb migrated to the anode.

With diammonium tartrate (0.015 *M*) plus tartaric acid (0.035 *M*), Ce(III) migrated as a cation, Eu and Pm as anions (Fig. 1). The separability and the sign of the ionic charge depended upon tartrate concentration and *pH*. Separability was not due to sorbability by the paper.

As determined by photography,<sup>6</sup> separation of many binary and ternary mixtures was complete. These mixtures included parents and daughters as Nd-Pm, Ce-Pr, Ba-La, and Sr-Y.

Combination of electrical migration with transverse flow of solvent, as previously described,<sup>3</sup> has now provided continuous separation of alkalis and alkaline earths from the rare earths. It has also yielded continuous separations of Y from Ce and of the rare earths from anions such as PO<sub>4</sub><sup>=</sup>.

(5) T. R. Sato, W. Kisielski, W. P. Norris and H. H. Strain, *Anal. Chem.*, submitted.

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#### THE PEROXIDE AND LIGHT INDUCED REACTIONS OF AMINES WITH OLEFINS: A ONE-STEP SYNTHESIS OF *d,l*-CONIINE

Sir:

A reaction of considerable potential usefulness in organic synthesis, the addition of alkyl amines to olefins, has been observed. In the presence of a peroxide, a condensation occurs between the  $\alpha$ -carbon atom of the amine and the olefin (the terminal carbon atom of 1-olefins) by what is probably a free-radical, chain reaction. For example, the reaction of piperidine with octene-1 in the presence of *t*-butyl peroxide gives 2-*n*-octylpiperidine, and *d,l*-coniine is obtained by the similar reaction of piperidine with propylene.

Under a pressure of nitrogen (25 lb./in.<sup>2</sup>), a reaction mixture containing piperidine (382. g., 4.50 moles, b.p. 105–106°, *n*<sub>D</sub><sup>20</sup> 1.4529), octene-1 (40 g., 0.36 mole, b.p. 120°, *n*<sub>D</sub><sup>20</sup> 1.4090), and *t*-

butyl peroxide (3 g.) was held at 120° for 50 hours. Additional peroxide (2 g. after 6 hours, 2 g. after 12 hours) was added. Distillation of the reaction mixture gave *t*-butyl alcohol (6.3 g., b.p. 80–82°), unreacted piperidine (359.5 g., b.p. 103–105°), octene-1 (9.5 g., b.p. 118–120°), and a product shown to be 2-*n*-octylpiperidine (31.7 g., b.p. 89° at 1 mm., *n*<sub>D</sub><sup>20</sup> 1.4589).

*Anal.* Calcd. for C<sub>18</sub>H<sub>27</sub>N: C, 79.11; H, 13.79; N, 7.10; mol. wt., 197. Found: C, 79.34; H, 13.81; N, 7.17; mol. wt., 190.

This product was identified by a comparison of its chemical and physical properties with 2-*n*-octylpiperidine (b.p. 89° at 1 mm., *n*<sub>D</sub><sup>20</sup> 1.4587) prepared (95% yield) by the dehydrogenation (over Adams catalyst in acetic acid solution) of 2-*n*-octylpyridine (prepared, 65% yield, by the reaction of  $\alpha$ -picoline, 111 g., 1.2 moles, with *n*-heptyl bromide, 71.6 g., 0.40 mole, and sodamide, 54 g., 1.39 moles).<sup>1</sup> The product gave a hydrochloride (m.p. 155–156°; m.p. of mixture with authentic sample, 155–156°).

*Anal.* Calcd. for C<sub>13</sub>H<sub>23</sub>NCl: C, 66.67; H, 12.07; N, 5.99. Found: C, 66.53; H, 12.16; N, 5.99.

Its reaction with phenyl isothiocyanate gave a thiourea derivative (m.p. 95°; m.p. of mixture with authentic sample, 95°). *Anal.* Calcd. for C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>S: C, 72.23; H, 9.70; N, 8.42. Found: C, 71.92; H, 9.56; N, 8.45.

A picrate (m.p. 78–80°) was also obtained. *Anal.* Calcd. for C<sub>19</sub>H<sub>30</sub>N<sub>4</sub>O<sub>7</sub>: N, 13.12. Found: N, 13.07.

The high boiling residue was distilled to give a fraction (b.p. 145–155° at 1 mm., *n*<sub>D</sub><sup>20</sup> 1.4683; 5.8 g., mol. wt. 299) presumed to have resulted from the condensation of one molecule of piperidine with two of octene-1. A residue (4.5 g., mol. wt. 448) remained. 2-*n*-Octylpiperidine (1 g.) was obtained in small yield when a solution containing piperidine (207 g., 2.44 moles) and octene-1 (20.5 g., 0.183 mole) was internally illuminated for 168 hours with a mercury discharge tube.

Piperidine (87. g., 1.03 mole) containing *t*-butyl peroxide (1.2 g.) was held at 125° for 12 hours under a pressure of propylene (30–40 lb./sq. in.). Additional peroxide (1.8 g.) was added as the reaction progressed. Distillation of the reaction mixture gave *d,l*-coniine (4 g., *n*<sub>D</sub><sup>20</sup> 1.4513, b.p. 93° at 70 mm.).<sup>2,3</sup> This product was identified by its hydrochloride (m.p. 211–212° uncor.) and its platinum chloride (m.p. 155–157° uncor.). Work to determine the scope and mechanism of this reaction is continuing.

(1) A. E. Tchitchibabin, *Bull. soc. chim.*, (5) 5, 429 (1938).

(2) E. Lellman and W. W. Muller, *Ber.*, 23, 684 (1890).

(3) A. Ladenburg, *ibid.*, 26, 855 (1893).

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#### STEROID RING CLOSURES USING THE ACYLOIN CONDENSATION

Sir:

We have found that the acyloin condensation in a homogeneous liquid ammonia-ether solution is an