the rare earth ions were precipitated as oxalates and the amount of reaction was then determined by titration with standard alkali.

0.5 N La^{3+} depresses the rate of decarboxylation by 10%. In the presence of the smaller Y^{3+} ion the rate of decarboxylation is equal within the experimental error of 4–5% to the rate of reaction in the absence of rare earth. On the basis of the salt effect of these diamagnetic ions the dysprosium ion, which is slightly larger than the yttrium ion, would be expected to give rise to a slightly slower rate of decarboxylation than that in the absence of rare earth or in the presence of Y^{3+}. In three sets of experiments the rate of reaction in the presence of 0.5 N Dy^{3+} was found to be 8, 10 and 13% faster than in the presence of 0.5 N Y^{3+}. The observed acceleration is tentatively attributed to the paramagnetic character of the dysprosium ion.

Investigations of the effect of paramagnetic ions on the decarboxylation of natural and isotopically substituted compounds are being continued.

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RECEIVED SEPTEMBER 28, 1953

SILICON TETRAFLUORIDE COMPLEX WITH ETHYLENEDIAMINE

Sir:

A recent report by C. J. Wilkins and D. K. Grant[1] of the preparation of two addition compounds of silicon tetrafluoride with one and with two molecules, respectively, of trimethylamine, has led us to add this note to the general subject of the coördinating power of the silicon halides. The fact that silicon assumes a coördination number of six in the fluosilicates, but is apparently unable to rise above four-coördination when chlorine atoms are employed as ligands, lends interest to the fact that in silicon tetrafluoride there is left sufficient room, as well as attractive force, about the silicon atom to accommodate one or even two molecules of trimethyl amine, with nitrogen the donor atom, as observed by Wilkins and Grant.

In following this general line of reasoning, we recently had prepared an addition compound of silicon tetrafluoride with ethylenediamine, the composition of which was determined by analysis and by molecular weight determinations as $SiF_4 \cdot CH_2NH_2NH_2CH_2$. No evidence of any other compound of the two reactants was obtained.

The ethylenediamine employed was twice redistilled from metallic sodium, and boiled within a range of 0.2°. The silicon tetrafluoride was prepared by thermal decomposition of precipitated barium fluosilicate, previously dried by heating at 200° for 3 hours in a vacuum of about 0.5 mm. The gas was preserved under pressure in a steel cylinder, and its properties agreed closely with the data given for pure silicon tetrafluoride by Jones, Kirby-Smith, Woltz and Nielson.[2]

The reaction of the vapors of anhydrous ethylenediamine, introduced into an evacuated flask to the limit of its vapor pressure at room temperature with gaseous silicon tetrafluoride, subsequently added, resulted in the formation of the white, solid complex and in a reduction of the pressure in the flask. More ethylenediamine was then admitted, followed by more silicon tetrafluoride. The quantity of liquid diamine added was measured by means of a buret; the tetrafluoride was measured in a gas buret over mercury. In one run, repetition of the procedure yielded 8 g. of a light, fine, white powder which was dried at 130°C. and 0.5 mm. for 3 hr. to free it of any excess diamine. At 0.2 mm. pressure the substance is sublimable about 225°. In other runs, smaller quantities were prepared. *Anal.* Fluoride, calcd., for $SiF_4 \cdot CH_2NH_2NH_2CH_2$ 46.35; found, 46.65%. Nitrogen, calcd., 17.08, found, 15.96%.

It is clear that in this compound a chelate structure is present, with ethylenediamine occupying two of the six coördination positions about the silicon atom. It is of interest that further addition of the diamine, even if coördinated in unidentate fashion, is apparently excluded by spatial considerations.

DEPARTMENT OF CHEMISTRY WALTER C. SCHUMB
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RECEIVED SEPTEMBER 3, 1953

RATE OF THE ELECTRON-TRANSFER EXCHANGE REACTION BETWEEN MANGANATE AND PERMANGANATE IONS[1]

Sir:

We have successfully measured the rate of the isotopic exchange reaction between $MnO_4^=$ and MnO_4^-. Other investigators,[2,3,4] employing higher reactant and/or sodium hydroxide concentrations than we have used, had found complete exchange in contact times considerably longer than ours.

Using the separation procedure developed by Bonner and Potratz[4] of extracting MnO_4^- into a chloroform solution of triphenylsulfonium bromide, we have followed the exchange starting either with tagged $MnO_4^=$ or with tagged MnO_4^-. Separation methods involving the coprecipitation of MnO_4^- with tetraphenylarsonium perchlorate or perrhenate have also been used successfully. Reactions were started and stopped by the rapid ejection of solutions from automatic pipets into solutions being mechanically stirred.

Figure 1 shows three of our best exchange curves. In each of these runs the concentrations of $MnO_4^=$ and MnO_4^- were approximately equal; precise values for the concentrations of the individual reactants are not known however, because appreciable reduction of MnO_4^- to $MnO_4^=$ occurred. The dependence of the half-time of the exchange in 0.15 f NaOH at 1° on the total reactant concen-

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(1) C. J. Wilkins and D. K. Grant, *J. Chem. Soc.*, 927 (1953).

(2) E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielson, *J. Chem. Phys.*, **19**, 242 (1951).

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(1) This work was supported by the National Science Foundation under grant G-196.

(2) W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

(3) H. C. Hornig, G. L. Zimmerman and W. F. Libby, *ibid.*, **72**, 3808 (1950).

(4) N. A. Bonner and H. A. Potratz, *ibid.*, **73**, 1845 (1951).