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.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
KENNETH S. PITZER
EDWARD GELLES

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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
MASSACHUSETTS INSTITUTE OF TECH.
CAMBRIDGE 39, MASS.
WALTER C. SCHUMB
PHILIP S. COOK

RECEIVED SEPTEMBER 3, 1953

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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).

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) 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).

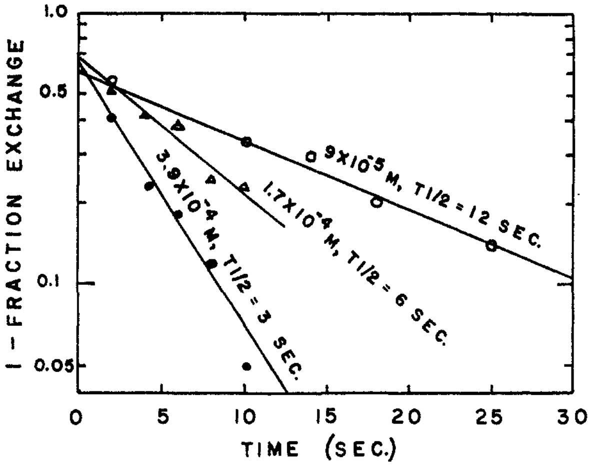

Fig. 1. Exchange curves 1°, 0.15*f* NaOH: concentrations are total manganese concentrations; $(C_6H_5)_3$ Br extraction separation used in the run at the intermediate concentration; $(C_6H_5)ReO_4$ coprecipitation separation used in the other two runs

tration is consistent with a second-order rate law with a constant of 650 M^{-1} sec.$^{-1}$.

In 2 *f* NaOH the rate of exchange is approximately twice that in 0.15 *f* NaOH, and the zero-time exchange is also greater. These observations are consistent with the nearly complete exchange in 15 seconds observed by Bonner and Potratz[4] for similar experimental conditions.

The fact that the rate of the exchange is small compared to collision frequencies shows that in aqueous solution the probability of electron transfer from $MnO_4^=$ to MnO_4^- is small, even though for these symmetrical reactants the Franck–Condon type restrictions are minimal.[5]

We hope to improve our technique sufficiently to make a detailed kinetic study of this exchange reaction.

[5] W. F. Libby, *J. Chem. Phys.*, **56**, 863 (1952).

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
ST. LOUIS 5, MISSOURI
JOHN C. SHEPPARD
ARTHUR C. WAHL

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REFRACTIVE INCREMENT OF THYMUS NUCLEIC ACID

Sir:

Recently we have had occasion to question the numerical value (0.160 ml.-g.$^{-1}$) of the refractive increment, d*n*/d*c*, of thymus nucleic acid (DNA), as published by Tennent and Vilbrandt in THIS JOURNAL[1] and cited by Smith and Sheffer,[2] Katz,[3] and Doty and Bunce.[4] We have measured the d*n*/d*c* of two samples of DNA prepared in our laboratory from fresh thymus tissue. Sample No. 1 was prepared by the method of Mirsky and Pollister[5]; the nucleoprotein of sample No. 2 was prepared in the same way as sample No. 1, but was deproteinized using the dodecyl sulfate denaturation described by Marko and Butler.[6] The samples were dissolved in the desired salt solution, stirred for at least 24 hours, and then dialyzed for several days against the salt solution, the dialysate being replaced occasionally.

The difference Δ*n* in index of refraction between the DNA solution and the last dialysate was in each case measured at 20°, using 4358 Å. light, by means of a differential refractometer. This instrument was somewhat similar to that described by Brice and Halwer[7] and was calibrated using data given by Stamm.[8] Using this calibration, a value of 0.178 ml.-g.$^{-1}$ was obtained for d*n*/d*c* of tobacco mosaic virus.

The concentration of each DNA sample was determined from its optical density at 2600Å. (measured by dilution into 0.1 *M* acetate buffer, *p*H 4.3), the ratio of density to phosphorus content for the sample and the per cent. phosphorus in DNA. For sample 1, the ratio of optical density (in 0.1 *M* acetate buffer, *p*H 4.3) in a 1-cm. cell to phosphorus was 6620 per mole of phosphorus/liter, and 6640 for sample 2. From data given by Sinsheimer and Koerner[9] on the nucleotide composition of DNA, it was computed that 9.35% by weight of the sodium salt of DNA is phosphorus.

Results are listed in the table:

DNA prepn.	Solvent	Δ*n*	Concn. in g./ml.	Δ*n*/*c*, ml.-g.$^{-1}$
1	0.1 *M* sodium acetate + 0.2 *M* sodium chloride, *p*H 5.7	0.701×10^{-4}	0.347×10^{-3}	0.202
	0.05 *M* sodium chloride	0.638×10^{-4}	0.323×10^{-3}	0.198
	0.001 *M* sodium chloride	0.599×10^{-4}	0.298×10^{-3}	0.201
2	0.1 *M* sodium acetate + 0.2 *M* sodium chloride, *p*H 5.7	1.63×10^{-4}	0.821×10^{-3}	0.199
	0.05 *M* sodium chloride	5.30×10^{-4}	2.62×10^{-3}	0.202
	0.001 *M* sodium chloride	1.68×10^{-4}	0.827×10^{-3}	0.204
			Av.	0.201

The combined effect on the observed Δ*n* of Donnan equilibrium and of the binding of NaCl by the DNA was computed from data given by Shack, Jenkins and Thompsett[10] for the case where the solvent was 0.05 *M* NaCl. It was found that because of these two effects, the observed Δ*n* of 5.30×10^{-4} may be too large by 1.9%. In making this calculation, it was necessary to assume that the polarizability of NaCl bound to the DNA is the same as that in a free solution of NaCl. For the other solvents the effect of salt binding and Donnan equilibrium cannot be calculated from the work of Shack, *et al.*, since they did not go to as low a NaCl concentration as 0.001 *M*, nor did they investigate the acetate buffered NaCl solution.

Since d*n*/d*c* enters to the second power in light-

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[3] S. Katz, THIS JOURNAL, **74**, 2238 (1952).

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[6] A. M. Marko and G. C. Butler, *J. Biol. Chem.*, **190**, 165 (1951).

[7] B. A. Brice and M. Halwer, *J. Opt. Soc. Am.*, **41**, 1033 (1951).

[8] R. F. Stamm, *ibid.*, **40**, 788 (1950).

[9] R. L. Sinsheimer and J. F. Koerner, *J. Biol. Chem.*, **198**, 293 (1952).

[10] J. Shack, R. J. Jenkins and J. M. Thompsett, *J. Biol. Chem.*, **198**, 85 (1952).