concentrations could not be used owing to the sparing solubility of the osmium(II) complex. The potentials found are shown in Table I. The potentials are generally higher than with the corresponding dipyridyl complexes, which in 0.1 *f* acid, for comparison, are, respectively, −1.07,[5] −1.288,[6] −0.856.[7]

TABLE I

Acid concn., *f*	$Fe(trpy)_2^{++}$/ $Fe(trpy)_2^{+++}$, v.	$Ru(trpy)_2^{++}$/ $Ru(trpy)_2^{+++}$, v.	$Os(trpy)_2^{++}$/ $Os(trpy)_2^{+++}$, v.
0.1	−1.076[a]	−1.281[a]	−0.9512[b]
0.2	−1.060	−1.263	−0.9414
0.5	−1.054	−1.219	−0.9250
1.0	−0.927	−1.202	−0.9070
2.0	....	−1.175	−0.8838

[a] ±0.002 v.
[b] ±0.0002 v.

The Standard Potential of the $Os(trpy)_2^{++}/Os(trpy)_2^{+++}$ System.—The potentials of oxidation–reduction mixture above, with the addition of potassium nitrate were measured at various ionic strengths at 25°. The plot of $I^{1/2}$ against E_h corrected, Table II, gave a straight line of slope 16.6 mv./0.1 unit of $I^{1/2}$. This compares with the calculated Debye–Hückel slope of 14.8 mv.[8] By extrapolation to $I = 0$, E_0 was found to be −0.9866 ± 0.0005 v. as compared with the $Os(dipy)_3^{++}/Os(dipy)_3^{+++}$ system[4] −0.8795 v.

TABLE II

$I^{1/2}$	E_h	E_h (cor.)
0.0474	−0.9773	−0.9786
0.0575	−0.9746	−0.9768
0.0652	−0.9726	−0.9759
0.0791	−0.9682	−0.9734
0.0908	−0.9677	−0.9711
0.1013	−0.9657	−0.9700

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The *cis–trans* Isomerization of $[Co(en)_2Cl_2]Cl$ in 2-Methoxyethanol

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In the course of some work with *cis*-$[Co(en)_2Cl_2]Cl$ it was observed that a solution of the salt in 2-methoxyethanol changed in color from purple to green. A study of the absorption spectra of the solutions showed that the color change was due to the rearrangement of the purple *cis*-isomer to the green *trans*-isomer. The kinetics of the reaction could be studied very easily with a spectrophotometer at 530 mμ. The isomerization was found to be followed by a slower reaction between the *trans*-isomer and the solvent to give unknown products.

An attempt was made to follow the reaction polarimetrically, but due to the high optical density of the *cis*-isomer at the NaD wave length it was not possible to obtain sufficiently large rotations for a kinetic study.

Experimental.—The *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ were prepared by the methods given by Bailar in "Inorganic Syntheses," Vol. II. They were washed with alcohol followed by ether, dried at 110°, and stored in a desiccator. The 2-methoxyethanol was Eastman Kodak Co. "Practical Grade." It was dried over anhydrous calcium sulfate and distilled into a dark glass stoppered bottle for storage.

Reagent grade KCl and $KClO_4$ were dried at 110° and used without further treatment. The 2-methoxyethanol solutions of these salts were prepared by shaking the solvent with the appropriate salt for about 10 hours at room temperature and then filtering off the excess solid. These solutions were analyzed by evaporating 5.00-ml. samples and weighing the residue of salt.

Solutions of the complex in the solvent were prepared by mulling the salt with a small amount of liquid. The slurry was then filtered through a sintered glass filter and the concentrated solution was diluted to a convenient concentration. The usual volume of solution used was from 30 to 50 ml. The concentration of the complex was determined colorimetrically at 530 mμ. The value of ϵ_{530} in the equation $O.D._{530} = \epsilon_{530} \times$ concn. (molar) × path length (cm.) was found to be (83.0 ± 1.6) O.D. units/millimole/cm.[2] This was shown to be valid up to 0.01 *M* solutions.

Optical density was measured with a Beckman DU spectrophotometer. Samples were pipetted from a reaction flask in the constant temperature bath directly into a 1-cm. Corex cell and immediately measured. The time was recorded at the moment the sample was withdrawn from the reaction flask. The entire operation took less than two minutes.

The temperature in the constant temperature bath was found to vary less than ±0.1° about the set temperature.

Because of the subsequent reaction between the solvent and the *trans*-isomer the data could not be treated by the usual simple first order expression. Satisfactorily reproducible results were obtained by plotting the log O.D. against time and drawing a straight line through the initial points. It was found that usually the first four or five points, extending over almost all of the first half-life, were fitted quite well by a straight line, from the slope of which the rate constant was calculated.

Results.—The rate constant for the reaction at 50° is not dependent upon the initial concentration of the complex, the chloride concentration, or the ionic strength of the solutions. This is shown in Table I. The evidence would seem to support an SN1 mechanism for the isomerization.

TABLE I

Concn. (*M*) of *cis*-c. × 10^3	Added salt	Ionic strength	$k \times 10^3$, min.$^{-1}$	Av.
2.92[a]	....	2.92	9.12	
3.52[a]	....	3.52	8.88	
5.12[a]	....	5.12	9.76	
5.71	....	5.71	9.63	(9.00 ± 0.73)
5.96[a]	....	5.96	9.76	× 10^{-3} min.$^{-1}$
6.66[a]	....	6.66	7.96	
7.69[a]	....	7.69	9.36	
7.77[a]	....	7.77	7.96	
1.59	$KClO_4$	58.7	9.00	
2.13	$KClO_4$	59.2	9.24	
5.53	$KClO_4$	62.6	9.49	(9.05 ± 0.26)
6.69	$KClO_4$	63.8	8.89	× 10^{-3} min.$^{-1}$
9.38	$KClO_4$	66.5	9.12	
11.9	$KClO_4$	69.0	8.77	
3.36	KCl	44.4	9.64	
5.23	KCl	46.2	8.45	(8.95 ± 0.62)
7.94	KCl	48.9	8.77	× 10^{-3} min.$^{-1}$

[a] Duplicate runs.

The rate constant was determined at four different temperatures from 30 to 50°. The results are summarized in Table II.

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TABLE II

$k \times 10^3$, min.$^{-1}$	Added salt	Ionic strength (approx.)	Temp., °C.
1.04	$KClO_4$	60	30.0
2.68	$KClO_4$	60	38.0
5.58	$KClO_4$	30	44.0
9.05	$KClO_4$	60	50.0

From the six possible combinations of pairs of *k* the activation energy in the Arrhenius expression is found to be 21.3 ± 2.7 kcal./mole, and the frequency factor is $(2.8 \pm 0.5) \times 10^{15}$ min.$^{-1}$.

This value for the activation energy is in good agreement with that reported by Brown, Ingold and Nyholm[2] for the same reaction in methanol solution, that is, 23.69 kcal./mole. The frequency factor was reported to be 3.05×10^{13} min.$^{-1}$. The close agreement of the activation energies for the reaction in different solvents is to be expected for a reaction of this type. The frequency factor, on the other hand, would be expected to be sensitive to the solvent. The small salt effect observed in methanol does not appear in 2-methoxyethanol although an effect of comparable magnitude should be discernible.

The fact that the *trans*-isomer is more stable than the *cis*-isomer can be explained by a simple electrostatic model. Two like charges located *cis* to each other on the vertices of a regular octahedron experience a greater mutual repulsion than if they are *trans* to each other. This is so even if one considers only the component of force directed along a line from the center of the octahedron through the vertex. This simple picture is shown to be inadequate, however, by the fact that 2-methoxyethanol solutions of *cis*-$[Cr(en)_2Cl_2]Cl$ do not isomerize to the *trans* form even after 30 minutes of refluxing. However, a solution of the *levo-cis*-isomer of the Cr complex, showing a rotation of +0.46° at the NaD line, was completely racemized after having been boiled for two minutes. Hence even though the bonds in the complex ion are loosened, as shown by the racemization, there are forces determining the geometry of the complex more powerful than the electrostatic repulsion between the chloride ions.

The reaction between *trans*-$[Co(en)_2Cl_2]Cl$ and 2-methoxyethanol has not been clarified. In boiling solvent it is rapid and after a short time an olive-green precipitate is formed. The solution becomes a more yellow-green in color. The precipitate is not soluble in 2-methoxyethanol, ethanol or ethyl ether. In water it is radically altered, giving a dark brown solution which yields a brown gummy material on evaporation. This brown solution will not give an AgCl precipitate with Ag^+ unless acidified. Analyses of the olive-green powder vary slightly from sample to sample and do not correspond to any rational empirical formula. Probably the material contains a polynuclear complex with some varying contaminants. A methanol solution of *trans*-$[Co(en)_2Cl_2]Cl$ in a sealed tube heated in the steam-bath for 12 hours gave no spectrophotometric evidence that a reaction had occurred.

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Reaction of Sodium Hydroxide with Methoxyfluoboric Acid and Monohydroxyfluoboric Acid

BY CHARLES M. WHEELER, JR., AND ROBERT G. NUTTLE

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Meerwein and Pannwitz[1] have reported the compounds sodium methoxyfluoborate, $NaBF_3OCH_3$, and sodium monohydroxyfluoborate, $NaBF_3OH$, prepared by the addition of an ether suspension of sodium methoxide and sodium hydroxide to boron trifluoride ethyl etherate. It should be pointed out that Booth and Martin[2] were incorrect in reporting the method used by Meerwein and Pannwitz in preparing these compounds. Neither compound was prepared by direct acid–base neutralization. This note reports results obtained in part of a general study of the preparation and properties of substituted fluoborates.

Experimental

Methoxyfluoboric acid and monohydroxyfluoboric acid were prepared by saturating methanol and water with boron trifluoride, after which the compounds were purified by fractional recrystallization.[3,4] Fluorine was determined by the calcium fluoride precipitation method of Ryss.[5] Boron was determined by carbonate fusion followed with mannitol–sodium hydroxide titration.

The X-ray powder diffraction photographs were made with copper radiation, filtered by nickel, using a Philips 57.3-mm. powder camera. The samples were mounted on Pyrex fibers. Intensities were estimated visually by comparison with a film of known intensity. Powder pattern data for sodium fluoborate have not been reported in the literature, although Klinkenberg[6] has reported lattice constants for this compound. Table I lists powder pattern data for sodium fluoborate.

Anal. Calcd. for $NaBF_4$: B, 9.85; F, 69.21. Found: B, 9.38, 9.52, 9.71; F, 69.11, 68.97, 69.17.

TABLE I

X-RAY POWDER DATA FOR SODIUM FLUOBORATE, "*d*" FOLLOWED IN PARENTHESES BY RELATIVE INTENSITY

3.80 (15), 3.39 (100), 3.13 (2), 2.83 (38), 2.73 (19), 2.55 (1), 2.31 (85), 2.19 (1), 2.14 (35), 2.03 (62), 1.99 (42), 1.90 (2), 1.83 (38), 1.80 (31), 1.71 (8), 1.69 (15), 1.61 (27), 1.55 (31), 1.49 (35), 1.46 (1), 1.39 (3), 1.36 (1), 1.36 (7), 1.33 (8), 1.31 (3), 1.28 (14), 1.24 (19), 1.20 (10), 1.13 (8), 1.09 (6), 1.07 (1), 1.05 (6), 1.02 (8), 1.01 (5), 0.997 (8), 0.983 (4), 0.967 (3), 0.956 (2), 0.944 (2), 0.925 (1), 0.912 (2), 0.902 (5).

Reaction of Methoxyfluoboric Acid with Sodium Hydroxide.—A saturated alcoholic (methanol) solution of sodium hydroxide was added slowly to methoxyfluoboric acid. Sufficient base was added to neutralize the acid, resulting in the formation of a precipitate. The solid product was filtered, washed and dried with acetone. A positive nitron test was obtained for the precipitate, with the nitron de-

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