exchange technique was used to separate 60–80% of the $CrCl^{++}$ from all of the Cr^{+++}.

The observed exchange must occur by a bridge activated complex[1] of the configuration $[Cr \cdots Cl \cdots Cr]^{+4}$ which permits transfer of chlorine. Electron transfer via other possible paths, whether by a single H_2O acting as a bridge or over a distance of several water molcules, or by a hydrogen atom transfer leads to net dissociation of $CrCl^{++}$[2]. The electron transfer is thus *very* much more efficient by the chloride bridged activated complex than by other available paths. Direct measurements show the rate of dissociation of $CrCl^{++}$ catalyzed by Cr^{++} to be lower by a factor of at least 10^4 than the measured exchange. At 0° in 1 *M* $HClO_4$, with $(Cr^{++}) = 6 \times 10^{-3}$ *M*, $(CrCl^{++})$ decreases by less than 1% in 2 hours. It is also of interest to note the specific rate of exchange in the system Cr^{++}–Cr^{+++}, $k \cong 0.025$ l. mole^{-1} min.$^{-1}$ at 27°.[3] A water molecule is probably the bridging group in the activated complex for this electron exchange.

It has been observed that Cr^{++} catalyzes the exchange of Cl^- and $CrCl^{++}$. This observation is remarkable in view of negligible catalysis of the dissociation of $CrCl^{++}$ by Cr^{++} and the immeasurably low rate of exchange of $CrCl^{++}$ and Cl^-. In *two* experiments at 0° in 1 *M* $HClO_4$, with $(Cr^{++}) = 5.3 \times 10^{-3}$ *M*, $(CrCl^{++}) = 0.048$ *M*, $(Cl^-) = 0.095$ *and* 0.024 *M*, first order dependence upon Cl^- is observed. The observed half times (31 min. and 48 min.) lead to a specific rate in a rate term $k'(Cr^{++})(Cl^-)(CrCl^{++})$ of 31 ± 1 l.^{2} mole^{-2} min^{-1}. The path is almost certainly the reverse of the reaction which has been studied previously.[1] Combination of the specific rates of the forward and reverse reaction leads to an estimate of 10^2 to 10^3 for $(CrCl^+)(Cl^-)/(CrCl_2^+)$, which seems reasonable.

$$CrCl_2^+ + Cr^{++} \underset{k'}{\rightleftharpoons} CrCl^{++} + Cr^{++} + Cl^-$$

Arguments which arise from (1) the necessity of preserving $CrCl^{++}$ in the forward reaction, and (2) making the activated complex readily accessible from Cr^{++}, Cl^- and $CrCl^{++}$ suggest the geometry $[Cr \cdots Cl \cdots Cr \cdots Cl]^{+3}$ for the activated complex. If this formulation is correct, the observations demonstrate that a negative ion can participate in an electron transfer process other than as a bridging group and that an unsymmetrical activated complex can provide a path for electron exchange.

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RECEIVED JULY 6, 1954

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(1) H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

(2) The equilibrium quotient $(CrCl^{++})/(Cr^{+++})(Cl^-)$ has the value 0.77 ± 0.06 at ionic strength 4.9 at 74° (H. S. Gates and E. L. King, unpublished work). Thus, the equilibrium dissociation of $CrCl^{++}$ under these experimental conditions is essentially complete.

(3) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(4) Acknowledging financial support by the Office of Naval Research.

(5) Acknowledging financial support by the U. S. Atomic Energy Commission.

RATE OF THE FERROCYANIDE-FERRICYANIDE EXCHANGE REACTION[1]

Sir:

The isotopic exchange reaction between the hexacyanoferrate(II) and hexacyanoferrate(III) ions has been the subject of numerous investigations.[2,3,4,5,6,7] In all except the first,[2] which is believed[3] to be in error because of a faulty separation procedure, complete exchange was observed in the time required to mix and separate the reactants. It was not known whether a very rapid exchange occurred prior to the separation or whether the exchange occurred during the separation. In our studies we have found both that the exchange is very rapid and that the separation-induced exchange is large, often complete.

We have investigated in greatest detail the separation method of Eimer and Dodson[7] in which about nine-tenths of the hexacyanoferrate(III) ion is extracted into a chloroform solution of tetraphenylarsonium chloride. We found the separation was effective at reactant concentrations as low as 10^{-6} to 10^{-7} *M*, but even at these low concentrations complete exchange occurred at 0° during the several seconds required to mix and separate the reactants. That complete exchange could occur during the separation process was shown by heterogeneous exchange experiments ($Fe(CN)_6^{-4}$ in the water phase, $Fe(CN)_6^{-3}$ in the chloroform phase) which were complete during shaking times of two seconds and less. This heterogeneous exchange can be slowed to measurable rates (half-times 10 seconds and longer) by addition of hexacyanocobaltate(III) ion in moderate concentrations.

It was found when the reactants were mixed in a 3-way stopcock[8] and the mixture injected directly into a chloroform solution 0.06 *f* in $(C_6H_5)_4AsCl$ and 0.002 *f* in $Co(CN)_6^{-3}$, that the exchange was incomplete. At 4° and reactant concentrations of 0.002 *M* the zero-time exchange was 75%. As the reaction time was lengthened by insertion of longer pieces of tubing between the stopcock and the chloroform, the per cent. exchange increased with a half-time of ~0.3 sec., which corresponds to a specific rate of ~10^3 moles/l./sec., if a second-order rate law is assumed.

Working at reactant concentrations in the range $(0.5\text{–}3) \times 10^{-4}$ *M* and starting and stopping the exchange by rapidly injecting the reactant and chloroform solutions into a tube containing a mechanical stirrer, we observed essentially complete

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(1) This research was started under the auspices of the U. S. Atomic Energy Commission by A.C.W. while a summer visitor at the Brookhaven National Laboratory during 1952. It has been continued at Washington University with the support of the National Science Foundation.

(2) S. Ruben, G. T. Seaborg and J. W. Kennedy, *J. Applied Phys.*, **12**, 308 (1941); reported by G. T. Seaborg, *Chem. Rev.*, **27**, 199 (1940).

(3) R. C. Thompson, THIS JOURNAL, **70**, 1045 (1948).

(4) W. B. Lewis, Tech. Report No. 19, O.N.R. Task Contract N5-ori-07806, "Isotopic Exchange by Electron Transfer Between Complex Ions," Mass. Institute of Tech., Jan., 1949.

(5) C. Haenny and E. Wikler, *Helv. Chim. Acta*, **32**, 2444 (1949).

(6) J. W. Cobble and A. W. Adamson, THIS JOURNAL, **72**, 2276 (1950).

(7) L. Eimer and R. W. Dodson, Brookhaven National Laboratory Quarterly Progress Report, (Oct. 1–Dec. 31, 1950), BNL 93 (S-8), p. 69.

(8) F. J. W. Roughton and G. A. Millikan, *Proc. Roy. Soc. (London)*, **A155**, 258 (1936).

zero-time exchange unless hexacyanoruthenate(II) ion also was added as carrier. At carrier concentrations of 0.002 M the zero-time exchange in several experiments was $\sim$60%, and the half-times of the homogeneous exchange reaction were in the range 2–5 sec. These half-times also are consistent with a specific rate of $\sim 10^3$ mole/l./sec., if a second-order law is assumed.

The reactions have been separated in the presence of carriers by coprecipitation of the hexacyanoferrate(II) ion with thallium(I) calcium hexacyanoruthenate(II) and with lead(II) hexacyanoruthenate(II). The zero-time exchanges were 85 and 80%, respectively. The progress of the exchange was followed using the latter separation procedure, and the rate observed is consistent with our other measurements.

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RECEIVED MAY 29, 1954

BOOK REVIEWS

Advances in Carbohydrate Chemistry. Volume 8. Edited by CLAUDE S. HUDSON, National Institutes of Health, Bethesda, Maryland, and MELVILLE L. WOLFROM, Department of Chemistry, The Ohio State University, Columbus, Ohio. Academic Press, Inc., 125 East 23rd Street, New York 10, New York. 1954. xvii + 408 pp. 16 × 23.5 cm. Price $10.00.

The current volume of these "Advances" opens on a sad note—the announcement of the death of its senior editor, Claude S. Hudson, on December 27, 1952. The book represents the final publication under his name and is truly a fitting culmination to his more than fifty years of productive research, writing and editing in the field of carbohydrate chemistry. In fact, Dr. Hudson had spent most of the day before his sudden and unexpected death editing manuscripts for this volume.

Volume 8 maintains the same high standards for its historical and critical reviews that had been set in the earlier numbers. The topics chosen seem to be particularly timely and to be of great usefulness for teachers, research workers and others whose interests lie in many fields of organic, bio and even industrial chemistry. The current issue is introduced by an obituary of Sir James Irvine, whose character and pioneering activities in carbohydrate chemistry have been outlined by E. L. Hirst, of The University, Edinburgh, Scotland.

The "Relative Reactivities of Hydroxyl Groups of Carbohydrates," (44 pp.), by James M. Sugihara, discusses configurational relationships and neighboring-group effects, selective etherification, selective esterification and hydrolysis, and selective oxidation of the hydroxyl groups in carbohydrates.

"The Chemistry of the 2-Desoxysugars" (61 pp.), by W. G. Overend and M. Stacey, describes the occurrence, detection and isolation of these biologically important substances, and then the methods that have been developed for the biosynthesis and chemical synthesis of the sugars, their *O*- and *N*-glycosides, phosphate esters and other derivatives. The relatively simple and inexpensive preparation of 2-deoxy-D-ribose from D-glucose that was announced by Dr. John C. Sowden in September, 1953, appeared too late for inclusion in this review.

"Sulfonic Esters of Carbohydrates" (109 pp.), by R. Stuart Tipson, is an exhaustive and critical treatise documented by about 1200 references to more than 500 original papers. It can be studied profitably by all of us who use "tosyl," "mesyl" or "nasyl" groups in our researches. Individual chapters cover the methods for sulfonylation, physical and chemical properties of the esters, reductive desulfonylation and desulfonyloxylation, the action of alkaline reagents, and the action of alkali metal halides and other salts on sulfonic esters.

"The Methyl Ethers of D-Mannose" (14 pp.), by G. O. Aspinall, continues the systematic cataloguing of the methyl ethers of sugars that was begun in volumes 5, 6 and 7 with D-glucose, D-galactose, the aldopentoses, L-rhamnose and the D- and L-fucoses. Syntheses and proofs of structure are included.

"The Chemical Synthesis of D-Glucuronic Acid" (19 pp.), by C. L. Mehltretter, and "D-Glucuronic Acid in Metabolism" (25 pp.), by H. G. Bray, form a natural pair of interesting articles. In the former will be found a description of the most satisfactory preparative method to date for D-glucuronolactone, while the latter is concerned mainly with the investigations into the origin of D-glucuronic acid and the mechanism of D-glucuronide formation.

"The Substituted-Sucrose Structure of Melezitose" (14 pp.), by Edward J. Hehre, may be considered an epilogue to the review on melezitose, by C. S. Hudson, that appeared in Volume 2. A major question had been raised by Dr. Hudson concerning the actual presence of the sucrose moiety in melezitose. In this article Dr. Hehre has described his own search for a specific hydrolytic enzyme, his success with several variants of *Proteus* bacteria, and his final isolation and identification of crystalline sucrose from melezitose.

"Composition of Cane Juice and Cane Final Molasses" (24 pp.), by W. W. Binkley and M. L. Wolfrom, summarizes the available data on the carbohydrates, enzymes, vitamins, nitrogen compounds, non-nitrogenous acids, pigments, waxes, sterols, lipids and inorganic components in the expressible juice from sugar cane and in the blackstrap or final molasses.

"Seaweed Polysaccharides" (36 pp.), by T. Mori, concludes Volume 8. Because of the growing interest and use of seaweed in food and industry, the varied carbohydrates derived from these algae have been the subject of many studies. This review deals mainly with the composition and structure of agar, the mucilage of *Dilsea edulis*, carrageenin from Irish moss and the similar mucilages of closely related seaweeds, fucoidin, laminarin and several other carbohydrates from seaweeds. For additional information, particularly on the preparation and industrial uses of these substances, the reader may be referred to the recent book "Polysaccharide Chemistry," by R. L. Whistler and C. L. Smart, by the same publishers (1953).

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Gegenstrom-Verteilung. By H. M. RAUEN and W. STAMM. Verlag von Julius Springer, Berlin W. 35, Reichpietschufer 20, West Berlin. 1953. vii + 81 pp. 15.5 × 23.5. DM. 12.80.

The majority of research workers who will find use for the method of "Countercurrent Distribution" are not particularly interested in the more technical aspects of the method. They will not wish to take time for a major study of this method of separation any more than of the other approaches such as chromatography, distillation, electrophoresis, etc., of which there is now such a vast literature. Yet no separation method can be used to best advantage without a basic