of the total S—F to C—F was found to be 1.0:2.8. The ^{19}F n.m.r. spectrum of V consisted of three peaks in the S—F, CF_3, and C—F regions having an area ratio of almost exactly 1:3:1, respectively.

The formation of the acyl fluoride discussed above probably involves the basic attack of the fluoride ion from potassium fluoride on the electropositive sulfur atom forming SO_2F_2 and the intermediate potassium alkoxy compound with subsequent formation of the acyl fluoride.

Acknowledgment.—This investigation was supported by Contract No. DA-01-021 ORD-11878.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Kinetics of Exchange of Chromium(II) Ion and Azidopentaaquochromium(III) Ion[1]

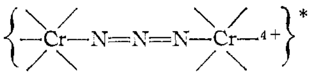
BY RICHARD SNELLGROVE[2] AND EDWARD L. KING[3]

Received August 3, 1963

Relatively rapid exchange of chromium atoms between chromium(II) ion and azidochromium(III) ion at 0° has been reported by Ball and King.[4] A more

$$CrN_3^{2+} + \overset{\otimes}{Cr}{}^{2+} = Cr^{2+} + \overset{\otimes}{Cr}N_3^{2+}$$

detailed kinetic study of this reaction as a function of temperature (0 to 36.4°) is the subject of the present note. The principal pathway for exchange in this temperature range involves the azide-bridged transition state



Experimental

Preparation of Reagents.—Acidic chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate in perchloric acid with amalgamated zinc. The resulting solution containing one-half mole of zinc ion per mole of chromium(II) ion was separated from the metallic zinc and stored under a positive pressure of nitrogen in a bottle closed with a self-sealing rubber gasket. Aliquots of the solution were removed with a syringe and hypodermic needle.

The chromium(II) ion was tagged with chromium-51 by addition of a relatively small amount of radioactive hexaaquochromium(III) ion; after several days, atoms of chromium-51 are randomly distributed between the two oxidation states of chromium.[5] The relatively small amount of tagged hexaaquochromium(III) ion does not interfere with the exchange experiments.

Azidochromium(III) ion was prepared and isolated by the procedure used earlier,[4] namely, oxidation of chromium(II) ion with iron(III) in an acidic solution containing azide followed by an ion-exchange separation of this species. In several preparations, the azide to chromium ratio ranged from 1.00 to 1.02. For analysis, solutions of azidochromium(III) ion were made alkaline, causing decomposition of the complex to give azide ion and chromite ion. The azide ion was oxidized in sulfuric acid solution by cerium(IV), the excess of which was titrated with standard iron(II) solution. Spectrophotometric analyses for chromium were performed after conversion to chromate ion by alkaline hydrogen peroxide.

Exchange Experiments.—Exchange experiments were performed by addition of tagged chromium(II) ion to deoxygenated perchloric acid solutions containing azidochromium(III) ion. At three to eight different times during each experiment, portions of reaction mixture were forced by nitrogen pressure into dilute acidic solutions containing iron(III) ion which quenched the exchange reaction by rapidly oxidizing chromium(II) ion to aquochromium(III) ion. After oxidation of the resulting iron(II) ion with hydrogen peroxide, azidochromium(III) ion (the only chromium species of charge +2) was separated from species of charge +3, chromium(III) ion and iron(III) ion, by elution from a column of Dowex-50 ion-exchange resin with 0.75 *M* perchloric acid. The specific activity of eluted azidochromium (III) ion was determined by combination of the chromium analysis as already described with a determination of radioactivity using a γ-ray spectrometer (scintillation detector).

During most kinetic experiments, one or more analyses for chromium(II) ion were made by delivering aliquots of reaction mixture into a solution containing iron(III) ion. Spectrophotometric analysis of the resulting solution for iron(II) using 1,10-phenanthroline allows calculation of the concentration of chromium(II) ion. The decrease of chromium(II) ion concentration during most experiments was slight.

The fraction exchange, f, was obtained by comparison of the specific activity of azidochromium(III) ion in the aliquots taken with the infinity-time specific activity calculated from the composition of the solution and the measured specific activity of the stock chromium(II) ion. Plots of log $(1 - f)$ *vs.* time were nicely linear for all experiments, indicating the absence of appreciable net chemical change. The straight line was not constrained to go through the origin. Most lines did, however, and the others intersected the $\log(1 - f) = 0$ axis within a few seconds of $t = 0$. Empirical second-order rate coefficients were calculated from slopes of these linear plots

$$k_2 = \frac{2.3\ \Delta \log (1 - f)}{([Cr^{2+}] + [CrN_3^{2+}])\Delta t}$$

Experimental Results

At each temperature in the range 0–36°, the empirical second-order rate coefficient was essentially independent of the concentrations of chromium(II) ion and azidochromium(III) ion. Therefore, in this temperature range the exchange is governed by the second-order rate law[6]

$$\text{exchange rate} = k_2[Cr^{2+}][CrN_3^{2+}]$$

Table I summarizes values of k_2. The mild dependence of this quantity upon acidity observed at 0° can be attributed to variation of electrolyte concentration.

At 0° the reaction of chromium(II) ion and *cis*-diazidochromium(III) ion *via* a double-bridged transition state[7] is ~45 times faster than the present reaction involving a single-bridged transition state. In contrast to this, the reaction[3] of chromium(II) ion

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[1] This work was supported in part by the United States Atomic Energy Commission under Contract AT(11-1)-1168.

[2] National Science Foundation predoctoral fellow 1959–1961.

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[4] D. L. Ball and E. L. King, *J. Am. Chem. Soc.* **80**, 1091 (1958).

[5] A. Anderson and N. A. Bonner, *ibid.*, **76**, 3830 (1954).

[6] The second-order rate coefficients for exchange observed in unreported experiments run in this work at temperatures in the range 38–50° were higher than expected from an extrapolation of the lower temperature results and appeared to depend upon the concentration of complex.

[7] R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).

TABLE I

THE RATE OF EXCHANGE OF CHROMIUM(II) ION AND AZIDOCHROMIUM(III) ION

$I \cong [H^+] = 0.5\ M$ (except as noted)

Temp., °C.	$[Cr^{2+}]$ $\times 10^3$ l. mole^{-1}	$[Cr(N_3)^{2+}]$ $\times 10^3$ l. mole^{-1}	$k_2 \times$ mole l.$^{-1}$ sec.
0	1.2	1.60	1.23
	1.4	1.60	1.24
	2.20	2.57	1.34
	3.45	1.25	1.32[a]
	4.2	1.60	1.39[a]
	1.4	1.50	1.48[b]
11.1	3.7	2.08	2.46
	3.8	1.40	2.40
	4.4	2.10	2.63
	6.5	2.10	2.56
20	1.1	2.12	4.94
	1.1	2.65	4.40
	2.6	1.40	4.70
28.9	1.15	2.65	7.7
	1.8	1.18	7.5[c]
	1.8	1.01	7.2
	2.8	1.35	6.0
36.4	1.55	1.40	12.9

[a] $I \cong [H^+] = 0.4\ M$. [b] $I \cong [H^+] = 0.9\ M$. [c] $[Zn^{2+}] = 0.02\ M$.

with fluorochromium(III) ion and with *cis*-difluorochromium(III) ion, each *via* a single-bridged transition state, have comparable rates, the reaction of fluorochromium(III) ion being ~2.5-fold faster.[4,8]

Comparison of the efficiently bridging azide ion and the more poorly bridging fluoride ion can be made through the activation parameters given below.

	ΔH^* $\times$ mole kcal.$^{-1}$	ΔS^* $\times$ mole deg. cal.$^{-1}$
$Cr^{2+} + CrN_3^{2+}$	9.6	−22.8
$Cr^{2+} + CrF^{2+}$	13.7[4]	−20.[4]

The above results indicate the enthalpy of activation to be primarily responsible for the difference.

The entropy of activation for exchange of chromium(II) and azidochromium(III) ions is very different from the value obtained by Bunn, Dainton, and Duckworth[9] for the exchange of iron(II) and iron(III) by a pathway involving azide ion. For the process

$$Fe^{2+} + \overset{\otimes}{Fe}N_3^{2+} = FeN_3^{2+} + \overset{\otimes}{Fe}{}^{2+}$$

they obtain a value of $\Delta S^* = +7.0$ cal. mole^{-1} deg.$^{-1}$ (the value of ΔH^* is 13.9 kcal. mole^{-1}) in the temperature range below 13°. At higher temperatures, the Arrhenius plot shows curvature giving rise to a lower activation energy and more negative entropy of activation. (Their reported values of the second-order rate coefficient at the highest two temperatures studied (15 and 27°) give $\Delta S^* \sim -24$ e.u.) However, it seems unwarranted to conclude that analogous mechanisms are responsible for the chromium reaction at 0–36° and the iron reaction at the high temperature extreme of the studies by Bunn, Dainton, and Duckworth.[9,10]

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(8) Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

(9) D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961).

(10) The apparent curvature in log *k vs.* 1/*T* plots at high temperatures observed in unreported experiments on the exchange of chromium(II) and azidochromium(III) ion (footnote 6) has the opposite sign to that observed in the iron system.

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Anhydrous Lithium Thiocyanate[1]

BY D. A. LEE

Received September 3, 1963

Lithium thiocyanate is the least stable of the alkali metal thiocyanates due to the large electrostatic deforming field of the lithium ion. It is extremely hygroscopic and there is good evidence that the solvent, tenaciously attached to the lithium ion, enhances LiSCN decomposition upon heating. Hydrated lithium thiocyanate has been prepared by several methods.[2] However, methods for dehydration have been unsuccessful, and no measurements have been recorded for the physical properties of anhydrous LiSCN. An obvious procedure for the preparation of anhydrous LiSCN would be to use anhydrous reactants; however, when this was attempted, using methanol solutions of KSCN and $LiNO_3$, the product included a double salt $LiK(SCN)_2$. Ether solutions, however, gave an etherate which could be desolvated by heating under reduced pressure.

Experimental

Hydrated LiSCN was prepared by mixing equal molar quantities of the solids $LiOH \cdot H_2O$ and NH_4SCN. When warmed, the mixture dissolved completely in the water of hydration of the $LiOH \cdot H_2O$. This solution was filtered, and the H_2O and NH_3 were removed by exposure to the vacuum pump and liquid N_2 trap at ~60°. When no more water distilled, the residue, which may still be liquid, was dissolved in about an equal volume of diethyl ether. This solution was filtered. To the filtrate was added 1.5–2 volumes of petroleum ether. (If sufficient water remains, two immiscible liquid phases will form.) A precipitate, corresponding in weight to $LiSCN \cdot (C_2H_5)_2O$, crystallized upon cooling and stirring. The etherate crystals were filtered with a minimum exposure to moist air, using a Büchner funnel. The ether in the crystals was removed under vacuum at 25°; the LiSCN was heated overnight to about 110° under vacuum. The product was redissolved in diethyl ether, crystallized with petroleum ether, and reprocessed by the procedure described above. The yield was usually about 90%. LiSCN was further purified by crystallization from diethyl ether. The product contained 9.9% Li, 88.5% SCN, and 0.09% H_2O by Karl Fischer determination. The m.p. was 281°.

The heat of fusion of LiSCN was determined by the method of mixtures using a calorimeter and furnace similar to that described by Goodkin, *et al.*,[3]; it was 5.0 ± 1.0 kcal./mole; the entropy of fusion was 9 ± 2 e.u./mole.

The change in volume on melting was determined by the dilatometric method similar to that of Plester, *et al.*[4] The volume change at the melting point corresponded to 2.58 ± 0.02 ml./mole. The density of LiSCN was 1.43 g./ml. at 26°.

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(1) This paper is based on work performed for the U. S. Atomic Energy Commission by Union Carbide Corporation.

(2) (a) F. A. Schimmel, *J. Chem. Eng. Data*, **5**, 519 (1960); (b) Gmelins Handbuch der Anorganischen Chemie, Lithium No. 20, Verlag Chemie, GMBH, Weinheim/Bergstrasse, 1960, p. 503.

(3) J. Goodkin, C. Solomons, and G. J. Janz, *Rev. Sci. Instr.*, **29**, 105 (1958).

(4) D. W. Plester, S. E. Rogers, and A. R. Ubbelohde, *Proc. Roy. Soc.* (London), **A235**, 469 (1956).