

Table I. Percentage Hydrolysis of Dinucleoside Phosphates^a

	Snake venom diesterase	Spleen diesterase
UpA ^b	100 (U, pA)	94 (Up, A)
UpA	25 (U, pA)	47 (Up, A)
ψpA	88 (ψ, pA)	69 (ψp, A)
ψpA	45 (ψ, pA)	35 (ψp, A)
CpU	93 (C, pU)	61 (Cp, U)
CpU	0	0
Cpψ	53 (C, pψ)	23 (Cp, ψ)
Cpψ	0	0
UpC	94 (U, pC)	100 (Up, C)
UpC	40 (U, pC)	80 (Up, C)

^a Ten absorbancy units (260 mμ) of each dinucleoside phosphate was incubated with snake venom phosphodiesterase^b (0.025 mg.) for 11 hr. at 37° in 0.02 M Tris acetate buffer (1.2 ml.) at pH 8.0 or with spleen phosphodiesterase^b (0.15 unit) for 2 hr. at 37° in 0.02 M ammonium acetate (1.2 ml.) at pH 6.0. The products of the enzyme digests are included in parentheses. In the spleen diesterase digests adenosine is usually obtained as inosine due to the presence of the contaminant deaminase. ^b UpA = uridine-(3'→5')-adenosine; UpA = UpA with a blocking group on the uridine moiety.

of these two diesterases. Snake venom phosphodiesterase is known to degrade polynucleotides in an exonuclease fashion, removing nucleotides in a stepwise manner from the 3'-hydroxyl end of the chain. Thus, all the compounds containing an unblocked nucleoside on the right-hand side are hydrolyzed by this enzyme (although those compounds containing blocks at the left-hand side are hydrolyzed more slowly than the parent dinucleoside phosphates from which they were derived). Resistance to the enzyme occurs when the block is present on the 3'-hydroxyl terminal base (CpU and Cpψ). The spleen diesterase is known to remove nucleotides in a stepwise fashion from the 5'-hydroxyl end of a polynucleotide chain. However, in contrast to the snake venom enzyme, this diesterase is capable of hydrolyzing dinucleoside phosphates where the block is located on the end at which the enzyme attacks but is unable to split those containing a block on the adjacent base.

Acknowledgment. This work was supported by the National Institutes of Health and the National Science Foundation.

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 Received July 27, 1965

The Preparation and Isomerization of the Sulfur-Bonded Monothiocyanate Complex of Chromium(III)¹

Sir:

It has been observed that thiocyanate ion is a much poorer bridging ligand than azide ion in many electron-transfer reactions.^{2,3} This has been ascribed to the fact that, in contrast to N₃⁻, the transfer of SCN⁻ in an inner-sphere reaction may yield an unstable isomer in which the "wrong end" of the thiocyanate is attached to the metal ion. For example, Ball and King² have

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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

(3) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

proposed that the CrNCS²⁺-Cr²⁺ exchange is slower than the CrN₃²⁺-Cr²⁺ exchange because transfer of thiocyanate produces the relatively unstable CrSCN²⁺, while transfer of azide produces a stable product. We have studied the oxidation of chromium(II) by iron(III) in the presence of thiocyanate ions⁴ and have established that CrNCS²⁺ and CrSCN²⁺ are produced in this reaction. We have also determined the spectrum of CrSCN²⁺ and some of its chemical properties.

The reactions were studied in 1 M perchloric acid at 25.0° on the flow apparatus which has been described previously.⁵ The following concentration ranges were used: (Cr²⁺) = 5.0 × 10⁻³ to 5.0 × 10⁻² M, [Fe(III)] = 5.0 × 10⁻⁴ to 1.0 × 10⁻² M, (SCN⁻) = 1.0 × 10⁻⁴ to 5.0 × 10⁻³ M. On mixing a solution containing Fe(III) and SCN⁻ with one containing excess Cr²⁺, three distinct changes in absorbance occur. These changes are most readily detected at 460 mμ (the maximum for FeNCS²⁺) and in the range 260 to 350 mμ (where iron(III) and the chromium(III) thiocyanate complexes have high molar absorbancy indices). The first change, which is due to the FeNCS²⁺-Cr²⁺ reaction, is too rapid to be followed on the flow apparatus even at reactant concentrations of 5 × 10⁻⁵ M ($k \geq 2 \times 10^7$ M⁻¹ sec.⁻¹). The second change in absorbance, of which only the tail is observed, is associated with the Fe³⁺-Cr²⁺, FeOH²⁺-Cr²⁺,⁶ and Fe³⁺-Cr²⁺-SCN⁻ reactions ($k = 2.3 \times 10^3$ M⁻¹ sec.⁻¹, 3.3×10^6 M⁻¹ sec.⁻¹, and $\sim 2 \times 10^5$ M⁻² sec.⁻¹, respectively). The final absorbance change corresponds to the chromium(II)-catalyzed isomerization of the CrSCN²⁺ produced in the first reaction ($k = 42 \pm 4$ M⁻¹ sec.⁻¹).⁷ The Fe³⁺-Cr²⁺-SCN⁻ reaction, which does not involve FeNCS²⁺ as a reactant, was studied by mixing solutions containing Cr²⁺ and SCN⁻ with solutions containing iron(III). These studies demonstrated that the CrSCN²⁺ was produced in the FeNCS²⁺-Cr²⁺ reaction and not in the oxidation of a chromium(II)-thiocyanate complex by iron(III).⁶ The latter reaction does, however, produce some CrNCS²⁺.

The FeNCS²⁺ is quantitatively converted into CrNCS²⁺ and CrSCN²⁺. This establishes that the FeNCS²⁺-Cr²⁺ reaction proceeds *via* an inner-sphere mechanism. It is difficult to determine the yield of CrSCN²⁺ exactly, but it appears to be about 35%. This estimate is based on two different analytical methods. The first involves reaction of CrNCS²⁺ and CrSCN²⁺ with chlorine; the isomers give Cr³⁺ and CrCl²⁺, respectively. In the second method Hg²⁺ is used to convert CrNCS²⁺ and CrSCN²⁺ to CrNCSHg⁴⁺ and Cr³⁺, respectively. The products of these reactions were separated by chromatography on a Dowex 50-X8 column.

A solution containing CrSCN²⁺ can be readily pre-

(4) The monothiocyanate complex of iron(III) is formulated as FeNCS²⁺. This structure has been suggested by S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16**, 1447 (1962), on the basis of infrared measurements, and also receives some support from the present studies.

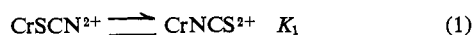
(5) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(6) G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964).

(7) The rapidity of the chromium(II)-catalyzed isomerization is probably responsible for the lack of success of earlier attempts [R. L. Carlin and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **6**, 217 (1958)] to prepare CrSCN²⁺ by the reaction of Cr²⁺ with Co(NH₃)₅NCS²⁺. It should be possible to prepare CrSCN²⁺ using this reaction by gradually adding a dilute chromium(II) solution to an excess of a concentrated Co(NH₃)₅NCS²⁺ solution. We have not yet attempted this.

pared by gradually adding a $5 \times 10^{-3} M$ Cr^{2+} solution to an equal volume of a well-stirred solution containing $5.5 \times 10^{-3} M$ Fe(III) and $4.5 \times 10^{-3} M$ SCN^- . Solutions prepared in this manner are green, while solutions of CrNCS^{2+} are purple.⁸ The absorption spectra of CrNCS^{2+} and CrSCN^{2+} are similar, except that the maxima in the spectrum of CrSCN^{2+} are shifted about 40 $m\mu$ toward longer wave lengths. The direction of this shift is expected⁹ on the basis of the weaker ligand field strength of sulfur-bonded compared to nitrogen-bonded thiocyanate and is additional evidence for the generally accepted view that the stable chromium(III) isomer is nitrogen bonded. Since the above solutions do not contain excess chromium(II) they are relatively stable. However, on standing the CrSCN^{2+} undergoes aquation (64%) and isomerization (36%) with an over-all rate constant of about $7.7 \times 10^{-5} \text{ sec.}^{-1}$.

If it is assumed that the exchange of chromium between Cr^{2+} and CrNCS^{2+} proceeds *via* remote attack by chromium(II),² then the equilibrium constant for the isomerization is simply the ratio of the rate constants



for the $\text{Cr}^{2+} + \text{CrSCN}^{2+}$ and $\text{Cr}^{2+} + \text{CrNCS}^{2+}$ reactions. Using the rate constant for the latter reaction determined by Ball and King² gives $K_1 = 3 \times 10^5$ at 25.0° and ionic strength 1.0 *M*. The nitrogen-bonded isomer is therefore about 7.5 kcal. mole⁻¹ more stable than the sulfur-bonded isomer.

Some relevant rate constants are presented in Table I. It is apparent from this table that the rate constants for the formation of the isomers from chromium(III)

Table I. Rate Constants for Some Chromium(III) and Iron(III) Reactions at 25.0° and $(\text{HClO}_4) = 1.0 M$

Reaction	k , $M^{-1} \text{ sec.}^{-1}$	Ref.
$\text{FeNCS}^{2+} + \text{Cr}^{2+}$	$\geq 2 \times 10^7$	This work
$\text{Fe}^{3+} + \text{Cr}^{2+} + \text{SCN}^-$	$\sim 2 \times 10^8$ ^a	This work
$\text{FeN}_3^{2+} + \text{Cr}^{2+}$	$\geq 2 \times 10^7$	This work
$\text{CrSCN}^{2+} + \text{Cr}^{2+}$	42	This work
$\text{CrNCS}^{2+} + \text{Cr}^{2+}$	1.4×10^{-4}	<i>d</i>
$\text{CrN}_3^{2+} + \text{Cr}^{2+}$	6.1 ^b	<i>e</i>
$\text{CrNCS}^{2+} + \text{H}_2\text{O}$	9.2×10^{-9} ^{b,c}	<i>f</i>
$\text{CrSCN}^{2+} + \text{H}_2\text{O}$	4.8×10^{-6} ^c	This work
$\text{Cr}^{3+} + \text{SCN}^-$	3×10^{-8}	This work
$\text{Cr}^{3+} + \text{NCS}^-$	1.8×10^{-6} ^b	<i>f</i>
$\text{CrSCN}^{2+} \rightarrow \text{CrNCS}^{2+}$	2.9×10^{-6} ^c	This work

^a Units are $M^{-2} \text{ sec.}^{-1}$. ^b Ionic strength = 0.5 *M*. ^c Units are sec.^{-1} . ^d Reference 2. ^e R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964). ^f C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

and thiocyanate differ by a factor of 60, while the rate constants for the dissociation of the isomers differ by a factor of about 10^4 . This shows that the difference in the stabilities of the isomers is due mainly to their rates of aquation. It may also be noted that, while the CrN_3^{2+} - Cr^{2+} exchange is faster than the CrNCS^{2+} - Cr^{2+} reaction, the exchange is not as fast as the CrSCN^{2+} -

(8) J. H. Espenson has also observed a green color near the end point of titrations of chromium(II) with iron(III) solutions containing thiocyanate (personal communication).

(9) C. E. Schäffer, Special Publication No. 13, The Chemical Society, London, 1959, p. 153.

Cr^{2+} reaction. This illustrates, among other factors, the importance of allowing for any differences in the standard free energy changes when comparing the rates of inner-sphere reactions.

Finally, these studies do not establish the structure of the stable monothiocyanate complex of iron(III) because the chromium(II) may attack the complex at either the adjacent or the remote position. However, the formation of CrSCN^{2+} suggests that the stable isomer of iron(III) is nitrogen bonded. If the stable isomer were sulfur bonded we would expect a 100% yield of CrNCS^{2+} provided remote attack on FeSCN^{2+} predominated over adjacent attack. However, this is by no means certain because adjacent attack might be more likely on the nonlinear FeSCN^{2+} than on the linear FeNCS^{2+} .

Further studies of the properties of CrSCN^{2+} and of unstable isomers produced in other oxidation-reduction reactions are in progress.

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Received July 21, 1965

The Role of the Triplet Excited State in the Photolysis and Radiolysis of Liquid Cyclopentanone¹

Sir:

We have reported previously² an interest in the correlation of the photolysis and radiolysis of cyclopentanone. The mechanism postulated by Srinivasan³ for the formation of 4-pentenal in the gas phase photolysis *via* a low vibrational level of an excited singlet state seemed to offer a unique system for study of excited states in radiation chemistry. In the Co-60 γ -radiolysis of liquid cyclopentanone, 4-pentenal has been found as a major primary product.^{4,5} According to the Srinivasan mechanism³ 4-pentenal should be the only major photolytic product in the liquid phase.

In recent investigations^{6,7} we have found that, with the exception of an oil, which may be a secondary product, 4-pentenal is the major primary photolytic product in liquid cyclopentanone. These studies were carried out at both 3130 and 2537 Å. and quantum yields for 4-pentenal were 0.37 ± 0.01 and 0.38 ± 0.02 , respectively. Minor primary products ($<< 1\%$) were found to be 1-butene and CO with 3130-Å. radiation and 1-butene, CO, ethylene, and cyclobutane at 2537 Å.

Additional experiments showed the 4-pentenal quantum yields to be insensitive to the addition of allyl alcohol, *n*-hexane, ethylene, carbon monoxide, 1-butene, DPPH, and low concentrations of ferric chloride. However, the 4-pentenal quantum yield was lowered

(1) This research was supported by the U. S. Atomic Energy Commission.

(2) M. Katayama, J. C. Whitmer, and C. N. Trumbore, *J. Am. Chem. Soc.*, **84**, 4025 (1962).

(3) (a) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); (b) S. Cremer and R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 4197 (1964).

(4) W. W. Bristowe, M. Katayama, and C. N. Trumbore, *J. Phys. Chem.*, **69**, 807 (1965).

(5) D. L. Dugle and G. R. Freeman, *Trans. Faraday Soc.*, **61**, 1174 (1965).

(6) P. Dunion, Ph.D. Thesis, University of Delaware, 1965.

(7) P. Dunion and C. N. Trumbore, to be submitted for publication.