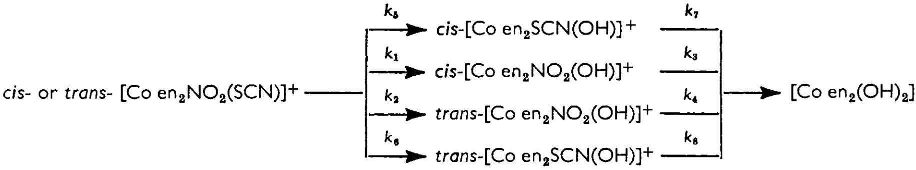
# **908.** *Nucleophilic Replacement at an Octahedrally Co-ordinated Metal Atom. Part II.*[1] *The Basic Hydrolyses of* cis- *and* trans-*Isothiocyanatonitrobisethylenediaminecobalt*(III) *Salts.*

By A. Rogers and P. J. Staples.

Basic hydrolysis of *cis*- and *trans*-$[Co\,en_2NO_2(SCN)]^+$ ions at 25°, 35°, and 45° has been studied and the Arrhenius parameters have been calculated. The main reaction is the replacement of the isothiocyanato-group, which is followed by the replacement of the nitro-group. In both cases, however, there is a small contribution from a reaction in which the nitro-group is replaced in the first step. The steric courses of the replacement of the isothiocyanato-group at 35° have been studied. In those substitutions in which the replacement of the isothiocyanato-group is the first step, *cis*-$[Co\,en_2NO_2(SCN)]^+$ yields 45—55% of *cis*-$[Co\,en_2NO_2(OH)]^+$, whilst *trans*-$[Co\,en_2NO_2(SCN)]^+$ yields 85—90% of *trans*-$[Co\,en_2NO_2(OH)]^+$. The rates of the basic hydrolysis of *cis*- and *trans*-$[Co\,en_2NO_2(OH)]^+$ and of *cis*- and *trans*-$[Co\,en_2(SCN)OH]^+$ at 35° are reported. The mechanisms of these reactions are discussed.

When *cis*- or *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) salts are dissolved in water no measurable replacement of either the isothiocyanato- or the nitro-group occurs at temperatures up to 45°. If, however, they are dissolved in sodium hydroxide solution the isothiocyanato-group is replaced readily. The hydroxonitro-compounds formed in this reaction are themselves then attacked to give dihydroxo-products. Simultaneously a small amount of the substrate reacts with the hydroxide ion, to yield *cis*- and *trans*-hydroxoisothiocyanatobisethylenediaminecobalt(III) ions which are subsequently attacked, yielding dihydroxo-products. The latter path constitutes only a small part of the overall reaction. The reactions may be summarised as follows:



The reactions at 25·0°, 35·0°, and 45·1° were studied. At each temperature the reaction was of the first order in complex. The rate was also linearly dependent on the hydroxide-ion concentration, but a plot of the apparent first-order rate constants against hydroxide-ion concentrations did not pass through the origin. This corresponds to a second-order basic hydrolysis accompanied by a small first-order background reaction, presumably aquation. Thus the rate is given by:

$$\text{Rate} = k_s[\text{Complex}][\text{OH}] + k_a[\text{Complex}].$$

Since the experiments were carried out in the presence of a large excess of hydroxide ion, the experimentally observed kinetics take the form:

$$\text{Rate} = k_f'[\text{Complex}],$$

where $k_f' = k_f + k_a$, $k_f$ = the pseudo-first order rate constant for pure basic hydrolysis, and $k_a$ = first-order rate constant for the background reaction. Direct measurement of the rate of this reaction at 35° was attempted but no detectable reaction was observed.

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[1] Staples, *J.*, **1963**, **3226**.

The fact that it could not be observed in neutral solution does not disprove its occurrence at pH 13.

It was shown that these reactions are not catalysed by light: reactions carried out in darkened vessels gave the same rate constants as those performed in clear vessels.

## RESULTS

*Replacement of Thiocyanate Ions from* cis- *and* trans-*Isothiocyanatonitrobisethylenediamine-cobalt*(III) *Salts.*—(*a*) *Kinetics.* The replacement of thiocyanate from these complexes has been studied by the method described in the Experimental section. It was shown that at the concentrations used neither the *cis-* nor the *trans*-complex formed an addition compound with silver nitrate. In some runs the complex ions present were removed on an ion-exchange column (sodium form) before the free thiocyanate ion concentration was determined. These runs gave the same results within experimental error. It was also shown that silver nitrate solution caused a slow removal of thiocyanate ion from *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) salts. This reaction was, however, too slow to interfere with the analytical procedure.

The Arrhenius parameters were evaluated from the corrected rate constants. The values obtained are: $E_{cis} = 30{\cdot}2$ and $E_{trans} = 31{\cdot}9$ kcal. mole$^{-1}$, log $A_{cis} = 18{\cdot}73$ and log $A_{trans} = 20{\cdot}04$, where $k = A \exp(-E/\boldsymbol{R}T)$.

TABLE 1.

Mean rate constants for the replacement of thiocyanate from *cis-* and *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) salts by hydroxide ions at different temperatures. [Rate constants calculated by plotting $\log_{10}(V_\infty - V_t)$ against time, where $V_\infty$ and $V_t$ are the silver nitrate titres calculated for ten half-lives and after time $t$, respectively.] *trans*-Isomer supplied as thiocyanate, *cis*-isomer as sulphate. For $k_f$ and $k_f'$ see text.

| Confign. | Temp. | [OH] (g.-ion l.$^{-1}$) | $10^5k_f'$ (sec.$^{-1}$) | $10^5k_f$ (sec.$^{-1}$) | $10^4k_8$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|---|
| *cis* | 25·0° | 0·1000 | 4·53 ± 0·13 | 4·33 | 4·33 |
| *cis* | 25·0 | 0·0750 | 3·36 ± 0·13 | 3·16 | 4·21 |
| *cis* | 25·0 | 0·0500 | 2·35 ± 0·03 | 2·15 | 4·30 |
| *cis* | 35·0 | 0·1000 | 21·8 ± 0·2 | 18·3 | 18·3 |
| *cis* | 35·0 | 0·0500 | 12·7 ± 0·2 | 9·2 | 18·4 |
| *cis* | 45·1 | 0·1000 | 108·5 ± 1 | 100 | 100 |
| *cis* | 45·1 | 0·0500 | 58·8 ± 0·6 | 50·3 | 101 |
| *trans* | 25·0 | 0·1000 | 4·91 ± 0·08 | 4·58 | 4·58 |
| *trans* | 25·0 | 0·0750 | 3·82 ± 0·10 | 3·49 | 4·65 |
| *trans* | 25·0 | 0·0500 | 2·56 ± 0·14 | 2·23 | 4·46 |
| *trans* | 35·0 | 0·1000 | 27·5 ± 0·3 | 22·0 | 22·0 |
| *trans* | 35·0 | 0·0500 | 16·7 ± 0·1 | 11·2 | 22·4 |
| *trans* | 45·1 | 0·1000 | 156 ± 1 | 138 | 138 |
| *trans* | 45·1 | 0·0500 | 88 ± 1 | 69·5 | 139 |

(*b*) *Steric course.* As at any given time there were seven coloured species present in the solution it was not possible to elucidate the steric course by spectrophotometry. It has, however, been possible to determine the steric course of thiocyanate replacement by a method previously described.[1] By following the change of nitrite-ion concentration with time it was possible to determine the steric course of the replacement of the isothiocyanato-group. The curves for possible steric courses were calculated by using the equation: [1]

$$\frac{[\mathrm{NO_2}^-]}{A_0} = 1 - \exp(-Kt - K't) - \frac{k_1}{K + K' - k_3}[\exp(-k_3t) - \exp(-Kt - K't)] - \frac{k_2}{K + K' - k_4}[\exp(-k_4t) - \exp(-Kt - K't)],$$

where $k_1$, $k_2$, $k_3$, etc., follow the notation of the reaction scheme (p. 4749). $K = k_1 + k_2$, $K' = k_5 + k_6$, and $A_0$ = the concentration of *cis-* or *trans*-$[\mathrm{Co\ en_2NO_2(SCN)}]^+$ at time zero.

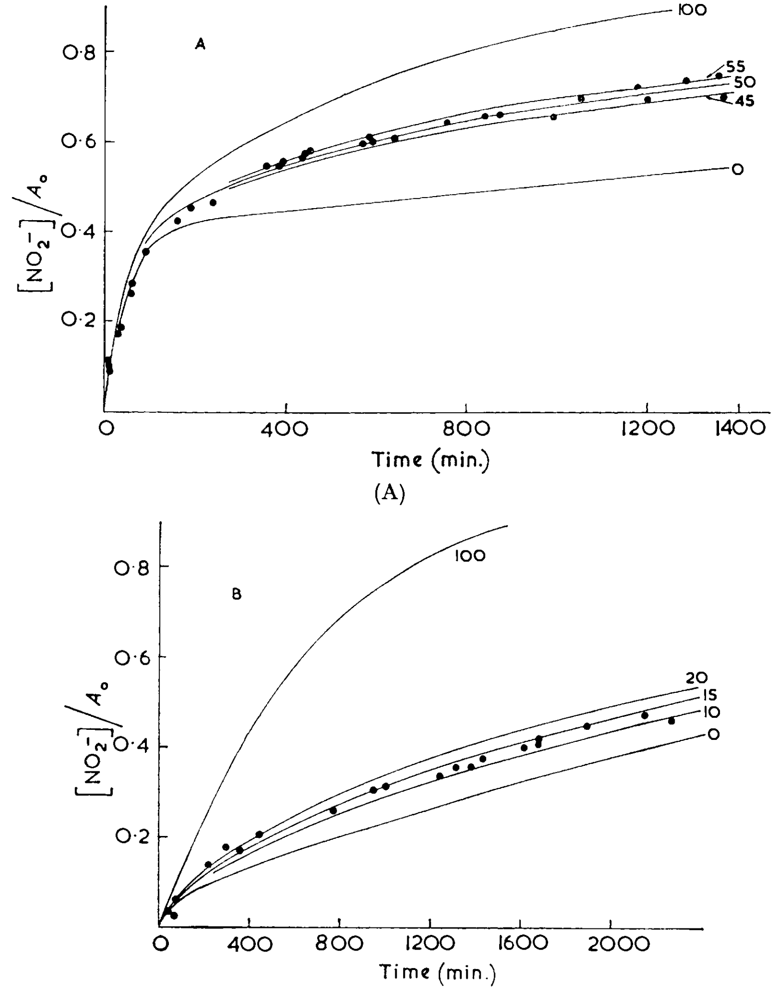
Since $K$, $K'$, $k_3$, $k_4$, $k_7$, and $k_8$ have been determined experimentally, by assigning arbitrary values to $k_1$ and $k_2$ such that $K = k_1 + k_2$, a family of curves corresponding to all possible

TABLE 2.

The pseudo-first-order rate constants (sec.$^{-1}$) used to calculate the steric courses of replacement of thiocyanate groups at 35·0°.

| *cis*-[Co $en_2NO_2(SCN)]_2SO_4$ | *trans*-[Co $en_2NO_2(SCN)$]SCN |
|---|---|
| $[OH^-] = 0{\cdot}1000$N | $[OH^-] = 0{\cdot}1000$N |
| $10^4K = 2{\cdot}18$; $10^4K' = 1{\cdot}48$; | $10^4K = 2{\cdot}75$; $10^4K' = 0{\cdot}20$; |
| $10^4k_3 = 0{\cdot}24_5$; $10^4k_4 = 0{\cdot}035$ | $10^4k_3 = 0{\cdot}24_5$; $10^4k_4 = 0{\cdot}035$ |

steric courses can be constructed. The steric courses were determined by fitting the experimental results for $[NO_2]/A_0$ against time to one of the family of curves (see Figs. A and B, the data for these are in Table 2).



Experimentally determined values of $[NO_2^-]/A_0$ (●) plotted against time for the basic hydrolysis of (A) *cis*-[Co $en_2NO_2(SCN)]^+$ and (B) *trans*-[Co $en_2NO_2(SCN)]^+$. The full lines show the various possible steric courses calculated by using the equation, and the figures on the lines indicate percentage of *cis*-compound.

The results indicate that the *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) complex reacts to yield 85—90% of *trans*-hydroxonitrobisethylenediaminecobalt(III) ion, but the *cis*-isothiocyanatonitro-reactant yields 45—55% of *cis*-hydroxonitro-complex.

It must be pointed out, however, that the rate constants used at 35° and at 0·1M-sodium hydroxide include the contribution from the background reaction, as they should, since it was not possible to measure directly the rate of basic hydrolysis in the absence of this contribution. For this reason the steric courses reported are not those for pure basic hydrolysis but are those for basic hydrolysis in the presence of a small, but not negligible, background reaction.

*Replacement of Nitrite Ion from* cis- *and* trans-*Isothiocyanatonitrobisethylenediaminecobalt*(III) *Salts. Kinetics.*—The replacement of the nitro-group has been followed by the method described in the Experimental section. It was not possible to determine the rate constants for these reactions from a logarithmic plot of $\log_{10}(a - x)$ against time. The rate constants were deduced from the initial slopes of plots of nitrite-ion concentration against time. The mean values of the rate constants at 350° evaluated by this method are: *cis*-isomer, $10^4k_s = 14{\cdot}8$ l. mole$^{-1}$ sec.$^{-1}$; *trans*-isomer, $10^4k_s = 2{\cdot}0$ l. mole$^{-1}$ sec.$^{-1}$.

As this reaction constituted such a small part of the total reaction its steric course could not be meaningfully deduced.

*Replacement of Thiocyanate Ions from* cis- *and* trans-*Hydroxoisothiocyanatobisethylenediaminecobalt*(III) *Salts by Hydroxide Ions.—Kinetics.* Replacement of thiocyanate ions from these complexes at 35° has been studied by the method described in a preceding section. These reactions were studied to enable the steric courses to be deduced at this temperature. The mean values of the rate constants obtained from several runs are: *cis*-isomer, $10^4k_s = 160$; *trans*-isomer, $10^4k_s = 4{\cdot}33$ l. mole$^{-1}$ sec.$^{-1}$.

It was also shown that these two hydroxoisothiocyanato-isomers did not rearrange at a measurable rate at pH 11 at 35°. Determination of the steric courses is, therefore, not complicated by the rearrangement of the monohydroxo-species formed in the first step.

*Replacement of Nitrite Ion from* cis- *and* trans-*Hydroxonitrobisethylenediaminecobalt*(III) *Salts by Hydroxide Ions.—Kinetics.* The replacement of nitrite ions from these complexes has been studied at 35·0° by the method described above. These rate constants were needed to evaluate the steric-course curves for the replacement of thiocyanate ions from *cis*- and *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) salts. The mean values of the rate constants from several runs are: *cis*-isomer, $10^4k_s = 2{\cdot}45$; *trans*-isomer, $10^4k_s = 0{\cdot}346$ l. mole$^{-1}$ sec.$^{-1}$.

It was shown that *cis*- and *trans*-hydroxonitrobisethylenediaminecobalt(III) salts did not rearrange at pH 11, so that the steric-course determinations were not complicated by rearrangement of the hydroxonitro-compounds.

## DISCUSSION

The results reported in the foregoing sections are collected in Table 3.

TABLE 3.

Rate constants, activation energies, and steric courses of the basic hydrolyses of some nitro- and isothiocyanato-bisethylenediaminecobalt(III) salts.

| Compound | Displaced group | Temp. | $10^4k_s$ (l. mole$^{-1}$ sec.$^{-1}$) | $E$ (kcal. mole$^{-1}$) | *cis*-Product (%) | Compound | Displaced group | Temp. | $10^4k_s$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| *cis*-$NO_2$(SCN) ... | SCN | 25·0° | 4·28 | | | *cis*-OH(SCN) ... | SCN | 35·0° | 160 |
| ,, ... | ,, | 35·0 | 18·3 | 30·2 | 45—55 | *trans*-OH(SCN) | ,, | 35·0 | 4·33 |
| ,, ... | ,, | 45·1 | 100 | | | *cis*-$NO_2$(SCN) ... | $NO_2$ | 35·0 | 14·8 |
| *trans*-$NO_2$(SCN) | ,, | 25·0 | 4·56 | | | *trans*-$NO_2$(SCN) | ,, | 35·0 | 2·0 |
| ,, | ,, | 35·0 | 22·2 | 31·9 | 10—15 | *cis*-OH($NO_2$) ... | ,, | 35·0 | 2·45 |
| ,, | ,, | 45·1 | 138 | | | *trans*-OH($NO_2$) | ,, | 35·0 | 0·346 |

The activation energies of the replacement of thiocyanate from *cis*- and *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) ions are not significantly different from each other but both are rather high. The few activation energies for basic hydrolyses that have been measured fall into two groups. In the first are reactions with activation energies of *ca.* 30 kcal. mole$^{-1}$, *e.g.*, of *cis*-chloroamminebisethylenediaminecobalt(III) salts,[2] and in

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[2] Pearson, Boston, and Basolo, *J. Phys. Chem.*, 1955, **59**, 304; Pearson, Meeker, and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 2673; *J. Inorg. Nuclear Chem.*, 1955, **1**, 342.

the second group are those with activation energies of *ca.* 23 kcal mole$^{-1}$, *e.g.*, of *trans*-chloroisothiocyanatobisethylenediaminecobalt(III) salts.[3] The reactions reported here belong to the former. The rates of basic hydrolysis of *cis*- and *trans*-chloronitrobisethylenediaminecobalt(III) salts are slower than those of the *cis*- and *trans*-chloroisothiocyanato-analogues. Asperger and Ingold[4] postulated that the reactions are comparatively slow because the chlorine atom must leave with its electron pair, *i.e.*, as a chloride ion. The nitro-group, however, exerts its strong electron-withdrawing influence so that departure of the chlorine atom, together with its lone pair, is inhibited. The results of the present investigation suggest that the nitro-group exerts its electron-withdrawing influence in these systems also. The rate of displacement of thiocyanate from *cis*- and *trans*-isothiocyanatonitrobisethylenediaminecobalt(III) salts is slower than that of thiocyanate ion from the *cis*- and *trans*-azidoisothiocyanato-[1] and *cis*-hydroxoisothiocyanato-analogues.[1]

More evidence for this electron-withdrawing power may be drawn from the steric course. The nitro-group apparently inhibits attack by hydroxide ions at those octahedral positions adjacent to itself because the electrons are polarised towards the nitro-group, and so inhibit nucleophilic attack at those positions. Asperger and Ingold[4] noted that the *trans*-chloronitrobisethylenediaminecobalt(III) ion yields 94% of *trans*-hydroxonitro-product, whilst the *cis*-chloronitro-complex yields 66% of *cis*-hydroxonitro-product. The steric course of basic hydrolysis of the two isothiocyanatonitrobisethylenediaminecobalt(III) ions are very similar to those of the chloronitro-analogues. The *cis*-isothiocyanatonitrobisethylenediaminecobalt(III) ion yields 45—55% of *cis*-hydroxonitro-product, whilst the *trans*-analogue yields 85—90% of *trans*-hydroxonitro-product.

## EXPERIMENTAL

*Preparations.*—*cis*- and *trans*-Isothiocyanatonitrobisethylenediaminecobalt(III) salts,[5] *cis*- and *trans*-aquonitrobisethylenediaminecobalt(III) salts,[4] and *cis*-[3] and *trans*-hydroxoisothiocyanatobisethylenediaminecobalt(III) salts[5] were prepared by recorded methods. The criteria of purity were analyses (see Table) and agreement of the visible and the ultraviolet absorption spectra of the samples with those of specimens of known purity.

| | Found (%) | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|
| Complex | C | H | SCN | $[SCN]^-$ | C | H | SCN | $[SCN]^-$ |
| *cis*-$[Co\ en_2NO_2(SCN)]_2SO_4$ ........... | 18·1 | 4·9 | 17·3 | — | 18·2 | 4·9 | 17·6 | — |
| *trans*-$[Co\ en_2NO_2(SCN)]SCN$ ......... | 21·3 | 4·8 | 33·9 | 16·9 | 21·3 | 4·7 | 34·2 | 17·1 |
| *cis*-$[Co\ en_2SCN(H_2O)]S_2O_6,3H_2O$ *†... | 12·95 | 5·3 | 12·5 | — | 12·8 | 5·2 | 12·4 | — |
| *trans*-$[Co\ en_2SCN(OH)]SCN,H_2O$ † ... | 21·5 | 5·6 | 34·9 | 17·4 | 21·8 | 5·7 | 35·2 | 17·6 |
| *cis*-$[Co\ en_2NO_2(H_2O)]SO_4$ ‡ ........... | 14·3 | 5·4 | — | — | 14·2 | 5·3 | — | — |
| *trans*- ,, ‡ ........... | 14·0 | 5·1 | — | — | ,, | ,, | — | — |

* Found: N, 14·75; S, 20·25. Required: N, 14·9; S, 20·5%. † Spectrum in ref. 3. ‡ Spectrum in ref. 4.

*Thiocyanate-ion Determination.*—Aliquot portions of the reaction mixture were passed through a column of Amberlite IR-120($Na^+$), and the effluent was acidified with dilute nitric acid. The free thiocyanate ions present in the effluent were titrated potentiometrically with standard silver nitrate solution, a silver wire and a calomel half-cell with an ammonium nitrate-agar bridge being used.

*Nitrite-ion Determination.*—Aliquot portions of the reaction mixture were passed through the above column, and the nitrite ions present in the effluent were estimated by Ridd's method.[6]

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[3] Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.
[4] Asperger and Ingold, *J.*, 1956, 2862.
[5] Werner, *Annalen*, 1912, **386**, 1.
[6] Ridd, Thesis, London, 1951.