Inorganica Chimica Acta, 68 (1983) 35–39

Base-Catalyzed Isomerization Reactions of Nitro- and Nitritobis(ethylenediamine)cobalt(III) Complexes in Aqueous Solution

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Received May 20, 1982

The linkage isomerization reactions of cis- *and* trans-*$Co(en)_2(ONO)_2^+$ were studied as a function of $[OH^-]$, temperature and pressure. The volumes of activation for the base-catalyzed isomerization processes were +19.7 ± 1.1 and +13.6 ± 1.2 cm^3 mol^{-1} at 25 °C for the* cis *and* trans *species respectively. The results are interpreted in terms of a conjugate-base mechanism, in line with earlier reported suggestions. The corresponding nitro complexes were shown to undergo slow* cis *to* trans *isomerization ($t_{1/2}$ ~ 20 hours at 86 °C) in neutral solution. No evidence for base-catalyzed* cis-trans *isomerization of $Co(en)_2(NO_2)_2^+$ could be found, due to the competing base hydrolysis processes.*

Introduction

In an earlier study [1] we reported mechanistic information on the spontaneous linkage isomerization reactions of *cis-* and *trans*-dinitritobis(ethylenediamine)cobalt(III) in aqueous acidic solution. The volumes of activation for these isomerization reactions are in close agreement with similar data reported [2] for the linkage isomerization reactions of species of the type $M(NH_3)_5ONO^{2+}$ (M = Co(III), Rh(III) and Ir(III)), and are considered as further evidence for intramolecular isomerization processes.

Recently, Sargeson and co-workers [3–5] detected base and metal ion catalysis for the linkage isomerization reactions of the above-mentioned pentaammine complexes. They [3] reported a volume of activation of +27 ± 1.4 cm^3 mol^{-1} for the base-catalyzed isomerization of $Co(NH_3)_5ONO^{2+}$, which differs completely from that reported for the corresponding spontaneous isomerization reaction [2], and was interpreted as evidence for a conjugate-base pre-equilibrium mechanism. In addition, evidence for intramolecular oxygen exchange during the spontaneous linkage isomerization process has also recently been reported [6]. These observations encouraged us to investigate the base-catalyzed linkage isomerization reactions of *cis-* and *trans-* $Co(en)_2(ONO)_2^+$, as well as the spontaneous and base-catalyzed *cis-trans* isomerization reactions of the corresponding nitro complexes.

Experimental

Cis- and *trans-*$[Co(en)_2(ONO)_2]ClO_4$ and -$[Co(en)_2(NO_2)_2]ClO_4$ were prepared as previously described [1, 7]. UV-visible absorption spectra were found to be in good agreement with those reported before [1, 8, 9]. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study. The ionic strength of the test solutions was adjusted with $NaClO_4$.

UV-visible spectra were recorded on a Perkin-Elmer 555 spectrophotometer. Kinetic measurements were performed on a Zeiss PMQ II spectrophotometer equipped with a thermostatted (±0.1 °C) high pressure cell [10] capable of housing the ‘pill-box’ cells [11]. Kinetic measurements were performed at convenient wavelengths, and the observed first-order rate constants were calculated in the usual way, for which the corresponding plots were found to be linear for at least two to three half-lives.

Results and Discussion

Base-Catalyzed Linkage Isomerization of Cis- *and* Trans-*$Co(en)_2(ONO)_2^+$*

Some preliminary measurements illustrated that the linkage isomerization reactions of *cis-* and *trans-* $Co(en)_2(ONO)_2^+$ are significantly catalyzed by OH^-, in agreement with similar results reported by Sargeson and co-workers [3, 4] for the analogous pentaammine complexes. Repetitive scan spectra of

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0020-1693/83/0000-0000/$03.00

TABLE I. k_{obs} as a Function of $[OH^-]$, Temperature and Pressure for the Linkage Isomerization Reaction of *cis*-$Co(en)_2(NO_2)$-ONO^+.[a]

Temp. °C	Pressure bar	k_{obs}[b] $\times 10^3$, sec^{-1}					$k_1 \times 10^3$ sec^{-1}	$k_2 \times 10^2$ M^{-1} sec^{-1}
		$[OH^-]$ = 0.02	0.04	0.06	0.08	0.10		
25.0	50	1.08	1.66	2.63	3.32	4.09	0.25 ± 0.10	3.84 ± 0.15
	200	0.99	1.51	2.20	3.00	3.37	0.33 ± 0.12	3.13 ± 0.19
	400	0.84	1.37	2.08	2.62	2.95	0.33 ± 0.12	2.74 ± 0.18
	600	0.82	1.20	1.73	2.41	2.62	0.31 ± 0.13	2.41 ± 0.19
	800	0.65	1.10	1.43	1.95	2.32	0.24 ± 0.05	2.09 ± 0.10
	1000	0.63	0.97	1.43	1.64	1.99	0.31 ± 0.07	1.69 ± 0.10
$\Delta V^{\neq}$, cm^3 mol^{-1}								+19.7 ± 1.1
10.0	50				0.32			
15.0					1.01			
20.0					1.93			
25.0					3.32			
30.0					7.00			
$\Delta H^{\neq}$, kcal mol^{-1}					24.5 ± 1.1			
$\Delta S^{\neq}$, cal K^{-1} mol^{-1}					12.7 ± 3.8			

[a] $[Co(III)] = 5 \times 10^{-3}$ *M*, wavelength = 322 nm, ionic strength = 0.5 *M*. [b] Mean value of at least two measurements.

the catalyzed isomerization of *cis*-$Co(en)_2(ONO)_2^+$ exhibited tendencies similar to those reported for the spontaneous isomerization process (see Fig. 1 of ref. 1). The first couple of spectra, recorded at 5 min intervals at 15 °C for a solution of the *cis* complex in 0.06 *M* NaOH, do not pass through the later produced isosbestic points at 405 and 458 nm, in close agreement with those found before [1]. This observation can be considered as evidence for a two-step process in which an initial fast isomerization reaction to produce *cis*-$Co(en)_2(NO_2)ONO^+$ is followed by a slower step to form *cis*-$Co(en)_2(NO_2)_2^+$. If older samples of the dinitrito complex are employed, no initial deviations occur and clean isosbestic points at 405 and 458 nm are observed. It has been observed [1, 12] that older samples of the complex had partially isomerized to produce the *cis*-nitronitrito species, explaining the observed effects. Kinetic measurements were, therefore, performed on older samples, such that the data in Table I are those for the second isomerization step.

Repetitive scan spectra of solutions of *trans*-$Co(en)_2(ONO)_2^+$ in 0.03 and 0.04 *M* NaOH at 11 °C exhibited clean isosbestic points at 414 and 492 nm from the start of the reaction. These differ to some extent from those observed [1] at 411 and 478 nm for the spontaneous isomerization process, for which it was concluded that the first isomerization reaction is rate-determining and is followed by a rapid second isomerization step. The different isosbestic points observed in basic medium may be an indication that the rate of the first isomerization step is accelerated to such an extent that it becomes of the same order as the second isomerization reaction, meaning that both steps are seen simultaneously. The corresponding activation parameters should provide more information on the validity of this suggestion. The kinetic data for the isomerization of *trans*-$Co(en)_2(ONO)_2^+$ is summarized in Table II.

The $[OH^-]$-dependence of k_{obs} in Tables I and II can be presented by

$$k_{obs} = k_1 + k_2[OH^-] \qquad (1)$$

in which k_1 presents the spontaneous and $k_2[OH^-]$ the base-catalyzed contribution towards the observed first-order rate constant. The values of k_1 and k_2, estimated according to a least square fit of the data, are also included in the Tables. It is obvious that the values of k_1 are subjected to considerable errors, especially in the case of the *trans* complex since the corresponding k_2 values are significantly larger than for the *cis* complex. Nevertheless, the values of k_1 are in good agreement with those extrapolated from the activation parameters for the spontaneous isomerization process reported elsewhere [12]. No effort was made to interpret the pressure dependence of k_1 due to the large error limits involved, and since this can be done more accurately by studying the spontaneous process separately [1].

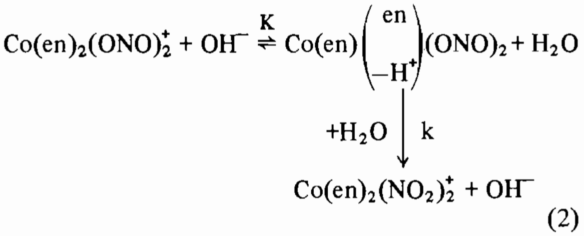
The values of k_2 in Tables I and II exhibit significant pressure dependences, and plots of $\ln k_2$ *versus*

TABLE II. k_{obs} as a Function of $[OH^-]$, Temperature and Pressure for the Linkage Isomerization of *trans*-$Co(en)_2(ONO)_2^+$.[a]

Temp. °C	Pressure bar	k_{obs}[b] × 10^3, sec^{-1} $[OH^-] = 0.02$	0.04	0.05	0.06	0.08	$k_1 \times 10^3$ sec^{-1}	$k_2 \times 10^2$ M^{-1} sec^{-1}
25.0	50	2.61	4.91	5.92	6.72	8.46	0.88 ± 0.26	9.68 ± 0.47
	200	2.23	4.39	5.28	6.09	7.97	0.46 ± 0.16	9.46 ± 0.29
	400	1.87	3.49	4.59	5.08	7.07	0.13 ± 0.19	8.60 ± 0.36
	600	1.59	3.14	4.10	4.49	6.14	0.14 ± 0.18	7.50 ± 0.34
	800	1.45	3.01	3.60	4.20	5.65	0.13 ± 0.10	6.90 ± 0.20
	1000	1.35	2.74	3.07	3.97	4.73	0.33 ± 0.24	5.69 ± 0.44
$\Delta V^{\neq}$, cm^3 mol^{-1}								+13.6 ± 1.2
6.0	50			0.22				
12.5				0.79				
18.0				1.75				
25.0				5.92				
30.6				10.06				
$\Delta H^{\neq}$, kcal mol^{-1}				25.8 ± 1.2				
$\Delta S^{\neq}$, cal K^{-1} mol^{-1}				17.7 ± 4.0				

[a] $[Co(III)] = 5 \times 10^{-3}$ *M*, wavelength = 335 nm, ionic strength = 0.5 *M*. [b] Mean value of at least two measurements.

pressure were found to be linear within the error limits concerned. The corresponding volumes of activation are positive, but significantly smaller than the value of 27 ± 1.4 cm^3 mol^{-1} reported [3] for the base-catalyzed isomerization of $Co(NH_3)_5ONO^{2+}$. A conjugate base mechanism was suggested to account for the base-catalyzed process in the latter study. We support this suggestion, and visualize the isomerization mechanism in the following generalized way



$$Co(en)_2(ONO)_2^+ + OH^- \overset{K}{\rightleftharpoons} Co(en)\left(\begin{matrix} en \\ -H^+ \end{matrix}\right)(ONO)_2 + H_2O \xrightarrow[k]{+H_2O} Co(en)_2(NO_2)_2^+ + OH^- \qquad (2)$$

The significantly different activation parameters reported for the base-catalyzed reactions (Tables I and II) as for the corresponding spontaneous processes [1], can be considered as further evidence for the suggested mechanism. The conjugate-base intermediate is capable of undergoing a significantly faster isomerization process than the protonated species. The suggested mechanism

$$k_{obs} = kK[OH^-]/\{1 + K[OH^-]\} \qquad (3)$$

reduces to $k_{obs} = kK[OH^-]$, since K is usually small [13]. If this was not the case, plots of k_{obs} *versus* $[OH^-]$ would have been curved. It follows that k_2 = kK, such that $\Delta V^{\neq}(k_2) = \Delta\bar{V}(K) + \Delta V^{\neq}(k)$. The volume of activation for the rate-determining isomerization step, *i.e.* $\Delta V^{\neq}(k)$, can only be estimated by making reasonable assumptions regarding the value of $\Delta\bar{V}(K)$.

If we consider the conjugate-base equilibration step in reaction (2) it is possible to estimate the overall volume change on the basis of the neutralization of H^+ (from the ammine ligand) and OH^- to produce H_2O, for which $\Delta\bar{V}$ = 22 cm^3 mol^{-1} at 25 °C [14]. This may be accompanied by a volume increase of approx. 2 cm^3 mol^{-1} due to deprotonation of the ammine [14], resulting in an overall $\Delta\bar{V}(K)$ value of *ca.* 24 cm^3 mol^{-1}. This value is slightly higher than the one assumed by Sargeson and co-workers [3]. It follows from a combination of the latter value and the activation volumes in Tables I and II that $\Delta V^{\neq}(k)$ equals −4 ± 1 and −10 ± 1 cm^3 mol^{-1} for the isomerization of the *cis*- and *trans*-complexes, respectively. These values seem to be realistic and in good agreement with those reported [1, 2] for the spontaneous linkage isomerization reactions of *cis*- and *trans*-$Co(en)_2(ONO)_2^+$ and $M(NH_3)_5ONO^{2+}$ (M = Co(III), Rh(III), Ir(III)). Furthermore, these values suggest that the isomerization reactions of the conjugate base intermediates follow the same reaction mechanism, most probably *via* a π-bonded intermediate as suggested before [1, 4, 6]. The significantly more negative value of $\Delta V^{\neq}(k)$ for the *trans* complex may indeed be an indication that both isomerization reactions occur simultaneously, as mentioned above.

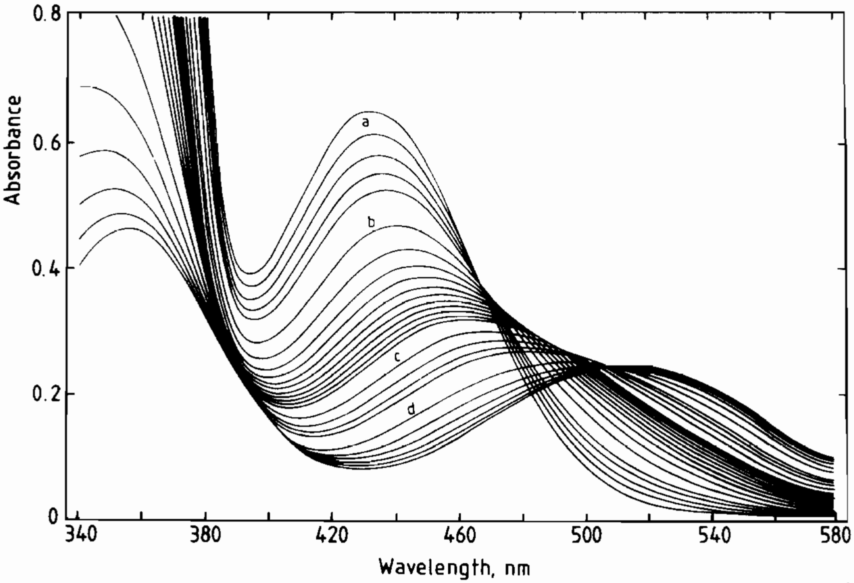


Fig. 1. Repetitive scan spectra for the base hydrolysis reaction of *trans*-$Co(en)_2(NO_2)_2^+$: [Co(III)] = 3.4×10^{-3} *M*; [NaOH] = 0.5 *M*; optical pathlength = 1 cm; temp. = 40 °C; time intervals: a = 5, b = 15, c = 60, d = 240 min.

The values of $\Delta V^{\neq}(k)$ differ considerably from the value of +5 cm^3 mol^{-1} reported by Sargeson *et al.* [3] for the base-catalyzed isomerization of $Co(NH_3)_5ONO^{2+}$. This value results from a significantly higher volume of activation (27 ± 1.4 cm^3 mol^{-1}) than found in the present study, and the authors do not give a reasonable explanation for its sign. The pressure dependence of the isomerization process was measured [3] at one $[OH^-]$, *viz.* 0.1 *M*, and the second-order rate constant for the base-catalyzed reaction path (k_{OH}) was determined by assuming appropriate literature values [2] for the spontaneous process (k_s). We prefer to interpret the $\ln k_{OH}$ *versus* pressure plot in terms of a linear relationship (within the error limits of such measurements) for which $\Delta V^{\neq}$ = 23 ± 1 cm^3 mol^{-1}. If, however, a data fit is performed on the experimentally observed values in 0.1 *M* NaOH, $\Delta V^{\neq}$ turns out to be 18.8 ± 1.0 cm^3 mol^{-1}, which is indeed very close to the value reported for the isomerization of the *cis*-nitronitrito complex in this study. Furthermore, this value results in a corresponding $\Delta V^{\neq}(k)$ value of −5 cm^3 mol^{-1} and correlates significantly better with the results of this and earlier studies [2].

Spontaneous and Base-Catalyzed Isomerization Reactions of Cis- *and* Trans-$Co(en)_2(NO_2)_2^+$

During the above reported investigation it was observed that secondary processes occurred subsequently to the linkage isomerization reactions in basic media. The rate of these processes were so slow that they did not interfere whatsoever with the investigated reactions. In our earlier study [1] we reported some peculiar observations concerning the isomerization reactions of $Co(en)_2(NO_2)_2^+$ in aqueous solution. We therefore undertook a more detailed investigation of these observations and studied the spontaneous and base-catalyzed isomerization reactions of $Co(en)_2(NO_2)_2^+$.

We previously [1] heated a 2×10^{-4} *M* aqueous solution of *cis*-$Co(en)_2(NO_2)_2^+$ for several days at 90 °C, and observed large spectral changes around 320 nm which could not be aligned with a *cis-trans* isomerization process. We repeated this experiment using a 5×10^{-3} *M* solution of the *cis* species and heating under reflux at 86 °C. Very distinct spectral changes were observed: the absorption maximum at 436 nm (ϵ = 197 M^{-1} cm^{-1}) shifted to 430 nm (ϵ = 193 M^{-1} cm^{-1}); and the absorption at 320 nm (ϵ = 3800 M^{-1} cm^{-1}) to 336 nm (ϵ = 3200 M^{-1} cm^{-1}) over a period of 4 days; clean isosbestic points were formed at 426 and 335 nm, respectively. These changes are in excellent agreement with that expected for a *cis* to *trans* isomerization process, with a corresponding half-life of *ca.* 20 hours at 86 °C. On longer heating further decreases in absorbance occurred, which in light of the results to be reported for the base-catalyzed process can be ascribed to a very slow aquation reaction. This also clarified our earlier observations, since for a dilute solution the aquation process will interfere to a greater extent with the isomerization process and make the latter unobservable.

Extended heating of a 5×10^{-3} *M* solution of *trans*-$Co(en)_2(NO_2)_2^+$ at 86 °C under reflux resulted in very minor spectral changes around 430 and 336 nm during the first four days. These are either due to some experimental errors introduced by the sample withdrawing procedure, or an indication for a minor reverse *trans* to *cis* isomerization component. However, during prolonged heating, significant absorbance decreases were observed over the following 15 days, and the results once again favour an aquation process.

Finally, we investigated the stability of *cis*- and *trans*-$Co(en)_2(NO_2)_2^+$ in basic medium in an effort to detect the possible base-catalyzed isomerization reaction. Repetitive scan spectra of *ca.* 4×10^{-3} *M* solutions of the complexes in 0.5 *M* NaOH at ~40 °C exhibited large spectral changes during the first couple of hours, followed by smaller changes during the next hours. No isosbestic points were formed, and the spectra clearly indicated a multi-step process. A typical example is given for the *trans* complex in Fig. 1. Both complexes produce identical final spectra with maxima at 355 and 518 nm, which were shown to be identical to those for an equilibrium mixture of *cis*- and *trans*-$Co(en)_2(OH)_2^+$ in a basic nitrite containing medium [15, 16]. The observed spectral changes can only be ascribed to hydrolysis of the dinitro and intermediate nitro-hydroxo complexes to produce the dihydroxo species [17]. The half-lives of the overall base hydrolysis processes were found to be of the order of 65 and 120 min at 39 °C (in 0.5 *M* NaOH) for the *trans*- and *cis*-complexes, respectively. The faster reaction for the *trans* complex is ascribed to the *trans* labilizing effect of the nitro ligand, and these results are in good agreement with earlier observations [17]. No information concerning possible base-catalyzed *cis* to *trans* isomerization of the dinitro complexes could be obtained from these spectral measurements, due to the dominating effect of the hydrolysis process.

Acknowledgements

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, and thank Dr. A. M. Sargeson for a preprint copy of ref. 5.

References

1 W. Rindermann, R. van Eldik and H. Kelm, *Inorg. Chim. Acta,* in press.
2 M. Mares, D. A. Palmer and H. Kelm, *Inorg. Chim. Acta, 27,* 153 (1978).
3 W. G. Jackson, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem., 19,* 904 (1980).
4 W. G. Jackson, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *J. Chem. Educ., 58,* 734 (1981).
5 W. G. Jackson, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Aust. J. Chem.,* to be published.
6 W. G. Jackson, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *J. Chem. Soc. Chem. Commun.,* 70 (1982).
7 W. Rindermann and R. van Eldik, *Inorg. Chim. Acta, 64,* L203 (1982).
8 F. Seel and D. Meyer, *Z. Anorg. Allg. Chem., 408,* 275 (1974).
9 F. Basolo, *J. Am. Chem. Soc., 72,* 4393 (1950).
10 F. K. Fleischmann, E. G. Conze, D. R. Stranks and H. Kelm, *Rev. Sci. Instrum., 45,* 1427 (1974).
11 W. J. le Noble and R. Schlott, *Rev. Sci. Instrum., 47,* 770 (1976).
12 F. K. Fleischmann, E. G. Conze, D. R. Stranks and H. (1974).
13 M. L. Tobe, 'Inorganic Reaction Mechanisms', Nelson, 95 (1972).
14 T. Asano and W. J. le Noble, *Chem. Rev., 78,* 407 (1978).
15 J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand., 6,* 1265 (1952).
16 S. Asperger and C. K. Ingold, *J. Chem. Soc.,* 2862 (1956).
17 J. B. Clarke, K. A. Pilkington and P. J. Staples, *J. Chem. Soc. (A),* 153 (1966).