# Kinetic and Isotopic Studies on the Reaction of Nitrous Acid with *cis*-Chlorobis(ethylenediamine)(hydroxylamine)cobalt(III)

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Nitrous acid reacts with the title complex giving $N_2O$ and $N_2$, the former gas being the major product. At $[H^+] > 0.1$ mol dm$^{-3}$ the rate law is Rate $\propto [H^+][HNO_2]$[complex], while at lower acidities the reaction is retarded by $H^+$ with a rate law: Rate $\propto [H^+]^{-1}[HNO_2]$[complex]. At $[H^+]$ *ca.* 0.1 mol dm$^{-3}$ there are deviations from these rate laws. The corresponding complex with *O*-methylhydroxylamine does not react with $HNO_2$. The reaction at higher acidities is assumed to involve rate-determining formation of an *O*-nitroso-species, $NH_2ONO$, which undergoes rearrangement to give a co-ordinated hyponitrite species which either decomposes to $N_2O$ or reacts *via* a nitrous acid-catalysed reaction to give $N_2$. The rate law containing the $[H^+]^{-1}$ term is less easy to interpret, and may involve attack of the nitrosating agent on a doubly deprotonated complex.

WE are interested in the reactivity of co-ordinated hydroxylamine [1] as part of our work on models [2] for hydroxylamine-dependent biological systems. A particularly well studied [3] reaction of hydroxylamine is that with nitrous acid to give $N_2O$, so accordingly we have examined the reaction of $HNO_2$ with the *cis*-chlorobis(ethylenediamine)(hydroxylamine)cobalt(III) cation. One feature of the nitrosation of hydroxylamine is the presence of reaction paths involving electrophilic attack on the oxygen atom of $[NH_3OH]^+$, implying that nitrosation of the co-ordinated hydroxylamine will occur despite the non-availability of the nitrogen lone pair to the nitrosating agent. The title complex was selected as it is one of the few well characterised inert hydroxylamine complexes, while the kinetics of its redox self-decomposition to give nitrogen and its aquation have been reported by Chan and Leh.[4] We failed to prepare complexes of the type $[Co(NH_3)_5(NH_2OH)][ClO_4]_3$.

## EXPERIMENTAL

The title complex was prepared by a modification of Berl's procedure.[5] A solution in water (48 cm$^3$) of $[NH_3OH]Cl$ (10.6 g) and sodium acetate (15.8 g) was added to finely powdered acid-free *trans*-$[Co(en)_2Cl_2]Cl$ (en = ethylenediamine) (50 g) with thorough stirring and cooling in an ice-tray. The stirring was continued until the solution was completely red in colour and had thickened to a paste. The solid complex (present as the chloride) was filtered off, washed with alcohol and diethyl ether, and recrystallised from 2 mol dm$^{-3}$ HCl. A concentrated solution (almost saturated) was made up in 2 mol dm$^{-3}$ $HNO_3$ and concentrated nitric acid slowly added dropwise until bright red crystals of *cis*-$[Co(en)_2Cl(NH_2OH)][NO_3]_2$ separated out. After recrystallisation from water, the product was washed with alcohol and diethyl ether and carefully dried (Found: C, 12.9; H, 5.20; Cl, 9.85; N, 25.8. Calc. for $C_4H_{19}ClCoN_7O_7$: C, 12.9; H, 5.10; Cl, 9.55; N, 26.1%). The i.r. spectrum confirmed that the hydroxylamine was *N*-bonded, and the stereochemistry [6] of the complex was *cis*. The corresponding complex with *O*-methylhydroxylamine was prepared similarly. **CAUTION:** Too rapid an addition of concentrated $HNO_3$ sometimes caused a very vigorous decomposition.

All the other reagents were of AnalaR grade or the next best grade available except for perchloric acid which was of Aristar quality. Prochem 95% $^{15}N$-labelled sodium nitrite was obtained from the British Oxygen Company.

Gaseous products of the reaction were analysed on an A.E.I. MS 20 mass spectrometer. Nitrite solution was placed in one leg of a Y tube and all the other components in the second leg. The solutions were thoroughly degassed by several (usually three) cycles of freezing to liquid-nitrogen temperature, evacuation, and warming prior to mixing.

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[1] M. N. Hughes and K. Shrimanker, *Inorg. Chim. Acta*, 1976, **18**, 69.

[2] M. N. Hughes and H. G. Nicklin, *Biochim. Biophys. Acta*, 1970, **222**, 650; *J. Chem. Soc. (A)*, 1971, 164.

[3] M. A. Hussain, G. Stedman, and M. N. Hughes, *J. Chem Soc. (B)*, 1968, 597 and earlier papers.

[4] S. C. Chan and F. Leh, *J. Chem. Soc. (A)*, 1967, 573.

[5] E. Berl, ' Untersuchungen über kobaltammoniak verbindungen,' Dissertation, Zurich, 1901.

[6] M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nuclear. Chem.*, 1966, **28**, 1659.

Kinetic runs were usually carried out at constant ionic strength (0.25 mol dm$^{-3}$, with sodium perchlorate) at 35.9 °C, and with a large excess of complex over nitrous acid (usually 100-fold). Runs were started by the addition of nitrite solutions to the otherwise complete reaction solution. The total volume of the reaction solution was 25 cm$^3$ and reaction vessels of 100 cm$^3$ capacity were used. Modification of either of these factors affected the rate of reaction slightly, a phenomenon probably related to the role of NO in the self-decomposition of $HNO_2$. Runs were followed by withdrawing samples at known time intervals and analysing for $HNO_2$ by a standard colorimetric method. This method was also used for determination of nitrous acid concentrations in stoicheiometry studies.

## RESULTS

*Stoicheiometry and $^{15}$N-Labelling Experiments.*—Visible and u.v. spectroscopic studies on the complex indicated that the aquachloro-complex was the product complex under all conditions. Studies over the range $[H^+] =$ 0.025—0.225 mol dm$^{-3}$ showed a *ca.* 1 : 1 consumption of $HNO_2$ and complex, with values of $-\Delta[NO_2^-]/-\Delta[\text{complex}]$ lying between 1.03 and 1.20, the higher values reflecting some self-decomposition of nitrous acid. The gaseous products include $N_2$, $N_2O$, and NO. The amount of NO produced is close to that obtained in independent assessments of the self-decomposition of $HNO_2$ under the exact experimental conditions, and so NO is not regarded as a product of the reaction. This is confirmed by the reduction in the amount of NO produced as the nitrous acid concentration is reduced, so at 0.000 5 mol dm$^{-3}$ $[HNO_2]$ less than 1% NO is obtained. While $N_2O$ is the major gaseous product, substantial amounts of dinitrogen (*ca.* 30%) are produced, thus representing a departure from the stoicheiometry of the reaction of the unco-ordinated hydroxylamine. While some $^{14}N{-}^{14}N$ is produced (probably by self-decomposition of the complex), most of the $N_2$ is $^{14}N{-}^{15}N$, showing that the nitrogen is a genuine product of the reaction. In Table 1 are shown details of the isotopic composition of the $N_2O$ produced in the reaction. It may be seen that it is made up of approximately equal amounts of $N_2O$ of mass numbers 44 and 45 and a small amount (8—16%) of $^{15}N^{15}NO$, implying a combination of two fragments derived from $HNO_2$. A detailed analysis of the isotopic data for $N_2$ is not presented in view of complications associated with analysing mixtures of $N_2O$ and $N_2$.

TABLE 1

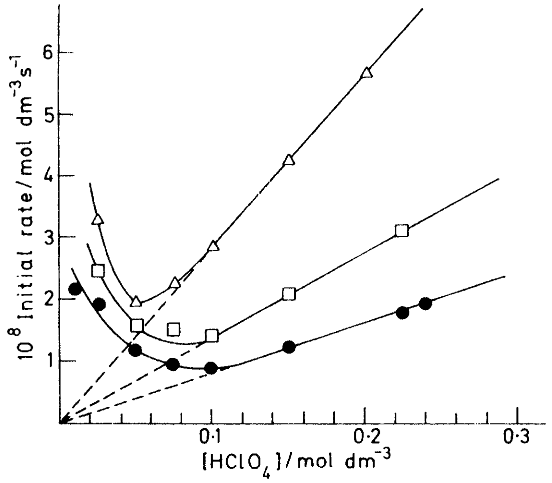
Isotopic composition (%) of $N_2O$ *

| $[H^+]$ mol dm$^{-3}$ | $[HNO_2]$ mol dm$^{-3}$ | $^{44}(N_2O)$ | $^{45}(N_2O)$ | $^{46}(N_2O)$ |
|---|---|---|---|---|
| 0.225 | 0.0100 | 37.2 | 53.7 | 9.1 |
| | 0.0020 | 41.9 | 41.7 | 16.4 |
| | 0.0005 | 40.6 | 45.3 | 14.1 |
| 0.025 | 0.0050 | 43.1 | 47.1 | 9.8 |
| | 0.0020 | 57.7 | 36.6 | 5.6 |
| | 0.0005 | 51.5 | 36.4 | 12.1 |

* [Complex] = 0.01 mol dm$^{-3}$. All the results are means from several determinations.

*Kinetics.*—The reaction was studied over the range $[H^+] = 0.01$—0.225 mol dm$^{-3}$ at several complex concentrations and usually $5 \times 10^{-5}$ mol dm$^{-3}$ $[HNO_2]$, the complex being in very large excess. Under certain conditions the reaction was clearly first order in the nitrous acid concentration, excellent linear plots of log *D* against time being obtained, while under other conditions good linear plots of *D* against time were obtained suggesting that the reaction was zero order in $[HNO_2]$. Intermediate situations were also found. Accordingly, initial rates or zero-order rate constants were measured for each run, together with the first-order rate constant where appropriate. The rate of reaction decreased with acidity from $[H^+] = 0.24$ to *ca.* 0.1 mol dm$^{-3}$ and then increased again as the acidity was decreased further. Results are shown in the Figure for three complex concentrations. The results at higher acidity may be extrapolated to zero acidity, going through the origin. Clearly this situation corresponds to an acid-catalysed reaction that is first order in $[H^+]$. Subtraction of these extrapolated values from the experimental values at acidities below $[H^+] = 0.05$ mol dm$^{-3}$ gives rate constants corresponding to a second term in the rate law that is retarded by acid, in practice having a dependence on $[H^+]^{-1}$.

As noted earlier, a complication arises regarding the order with respect to $HNO_2$. At the low and high ends of the acidity range covered the reaction is first order with respect to $[HNO_2]$; thus at $[H^+] = 0.225$ mol dm$^{-3}$ the first-order rate constant remained constant over a ten-fold variation in $[HNO_2]$. As the acidity approaches the value corresponding to the minimum reaction rate so the order in $[HNO_2]$ decreases, and over the acidity range *ca.* 0.05—0.10 mol dm$^{-3}$ is apparently zero. In addition, at higher acidities large increases in $[HNO_2]$ result in a tendency to second-order kinetics in $[HNO_2]$. This phenomenon may be understood readily by the incursion into the rate law of a term corresponding to nitrosation by $N_2O_3$, but no attempt was made to study it further. Kinetic results are shown in Tables 2 and 3, in which details are given of the dependence of the initial rate ($k_0$) on $[H^+]$, $[HNO_2]$, and [complex], although some values of $k_1$, the first-order rate constant, are given where appropriate. Successive half-lives are also given to indicate the order with respect to $[HNO_2]$. The reaction is shown to be first order in $[H^+]$, at each complex concentration, for $[H^+] \geqslant 0.075$ mol dm$^{-3}$ since values of $k_0/[H^+]$ are constant. The reaction is also first order in [complex] as shown by the fairly good constancy of $k_0/[H^+][\text{complex}]$. Since the reaction is also clearly first order in $[HNO_2]$ at higher acidities, the rate



Dependence of initial rate on acidity at 35.9 °C. [complex] = 0.02(△), 0.01(□), and 0.005 mol dm$^{-3}$ (●)

law is thus represented by equation (1), where $k_1$ is the first-order rate constant, $k_2 = k_1/[\text{complex}]$, and $k_3 = k_2[\text{H}^+] = 3 \times 10^{-1}$ dm$^6$ mol$^{-2}$ s$^{-1}$ at 35.9 °C.

$$\text{Rate} = k_3[\text{H}^+][\text{HNO}_2][\text{complex}] \qquad (1)$$

Fewer results are available at lower acidities, but inspection of the values of the initial rates $k_0 - k_{\text{ex.}}$ (where $k_{\text{ex.}}$ is the initial rate of the acid-catalysed reaction, obtained by extrapolation) indicates that the rate law for the acid-retarded reaction approximates to (2).

TABLE 2

Dependence of rate on $[\text{H}^+]$ and [complex] at $[\text{HNO}_2] = 5 \times 10^{-5}$ mol dm$^{-3}$, 35.9 °C, and $I = 0.25$ mol dm$^{-3}$

| [complex] | $[\text{H}^+]$ | $10^8k_0$ (Initial Rate) | $t_{\frac{1}{2}}$ | Order in $[\text{HNO}_2]$ [a] | $10^7k_0/[\text{H}^+]$ [b] |
|---|---|---|---|---|---|
| mol dm$^{-3}$ | | mol dm$^{-3}$ s$^{-1}$ | min | | s$^{-1}$ |
| 0.02 | 0.200 | 5.69 | 10.0, 10.4 | 1 | 2.85 |
| | 0.150 | 4.27 | 13.2, 14.2 | 1 | 2.85 |
| | 0.100 | 2.85 | 19.6, 14.4 | 0.6 | 2.85 |
| | 0.075 | 2.25 | 21.8, 15.2 | 0.5 | 3.00 |
| | 0.050 | 1.96 | 22.2, 11.4 | 0 | |
| | 0.025 | 3.29 | 15.0, 9.8 | 0.4 | |
| 0.01 | 0.225 | 3.09 | 19.5, 19.0 | 1 | 1.37 |
| | 0.150 | 2.11 | 26.5, 23.5 | 1 | 1.41 |
| | 0.100 | 1.34 | 45.5, 24.0 | 0 | 1.34 |
| | 0.075 | 1.52 | 39, 23.5 | 0.3 | |
| | 0.051 | 1.57 | 35, 18 5 | 0 | |
| | 0.025 | 2.45 | 27, 16 | 0.3 | |
| 0.0075 | 0.225 | 2.36 | 28, 28 | 1 | 1.04 |
| 0.005 | 0.240 | 1.94 | 27, 26 | 1 | 0.81 |
| | 0.225 | 1.78 | 28, 24 | 1 | 0.79 |
| | 0.150 | 1.26 | 39, 29.5 | 0.6 | 0.84 |
| | 0.100 | 0.86 | 51, 25 | 0 | 0.86 |
| | 0.075 | 0.96 | 49, 24 | 0 | |
| | 0.050 | 1.16 | 43, 28 | 0.4 | |
| | 0.025 | 1.89 | 28, 22 | 0.7 | |
| | 0.010 | 2.15 | 26, 24 | 1 | |

[a] Calculated from successive $t$ values. [b] Values of $k_0/[\text{H}^+]$ are given for acidities for which the acid-catalysed path is dominant. Mean values given below.

| [complex] | $10^7k_0/[\text{H}^+]$ | $10^5k_0/[\text{H}^+][\text{complex}]$ |
|---|---|---|
| mol dm$^{-3}$ | s$^{-1}$ | dm$^3$ mol$^{-1}$ s$^{-1}$ |
| 0.020 | 2.89 | 1.44 |
| 0.010 | 1.39 | 1.39 |
| 0.0075 | 1.04 | 1.38 |
| 0.0050 | 0.825 | 1.65 |

$$\text{Rate} = k_3{}^*[\text{H}^+]^{-1}[\text{HNO}_2][\text{complex}] \qquad (2)$$

$D_2O$ *effect.* The effect on the rate of carrying out the reaction in $D_2O$ was examined at 35.9 °C, $[\text{HNO}_2] = 5 \times 10^{-5}$, $[\text{complex}] = 5 \times 10^{-3}$, and $[\text{H}^+] = 0.060\,8$ and 0.156 mol dm$^{-3}$. Values of $k_{\text{H}}/k_{\text{D}}$ were 3.2 and 3.00 respectively. The result at higher acidity may reflect kinetic and equilibrium factors since $[\text{D}_2\text{NO}_2{}^+] = 2.2[\text{H}_2\text{NO}_2{}^+]$,[7] in which case the true kinetic-isotope effect is 6.6.

TABLE 3

Dependence of rate on $[\text{HNO}_2]$ at [complex] = 0.005 mol dm$^{-3}$ and 35.9 °C

| $[\text{H}^+]$ | $10^5[\text{HNO}_2]$ | $10^4k_1$ |
|---|---|---|
| mol dm$^{-3}$ | | s$^{-1}$ |
| 0.225 | 100 | 5.32 |
| | 75 | 5.60 |
| | 50 | 5.00 |
| | 25 | 5.12 |
| | 10 | 4.48 |
| | 5 | 4.32 |
| 0.025 | 100 | 1.29 |
| | 75 | 1.25 |
| | 50 | 1.28 |
| | 25 | 1.26 |

*Catalysis by* $[\text{SCN}]^-$. This anion catalyses nitrosations *via* the formation of NOSCN, a carrier of $[\text{NO}]^+$. Accordingly, the effect of $[\text{SCN}]^-$ was studied for both the acid-catalysed and -retarded reactions in the hope that different results might be observed for the two paths. Initially, at $[\text{H}^+] = 0.225$ mol dm$^{-3}$, thiocyanate showed a considerable catalytic effect. Rate constants for the catalysed reaction obtained by subtracting values at $[\text{SCN}^-] = 0$ showed a first-order dependence on $[\text{SCN}^-]$. However, the use of a second batch of complex indicated that $[\text{SCN}^-]$ retarded the reaction, in some cases nitrite actually being produced instead of being consumed, thus accounting for the apparent retardation of loss of nitrite in other cases. The production of nitrite could be explained by the oxidation[8] of thiocyanate by $\text{HNO}_2$ and nitrate (the anion of the complex), but clearly this reaction seems to be further catalysed by some impurity in the complex, a point worthy of future investigation. The values of $k_1$ at $[\text{SCN}^-] = 0$ were independent of the batch of complex used.

*Reaction with cis-*$[\text{Co(en)}_2\text{Cl(NH}_2\text{OMe)}][\text{NO}_3]_2$. Similar studies were attempted on the reaction between $\text{HNO}_2$ and the *O*-methylhydroxylamine complex. However, it is clear that the only reaction proceeding is that involving the self-decomposition of nitrous acid, as confirmed by comparison with blank runs without complex. Some runs were attempted with equimolar concentrations of reactants and after standing for *ca.* 20 h, concentrated $\text{HClO}_4$ was added to precipitate the complex. This analysed as $[\text{Co(en)}_2\text{Cl(NH}_2\text{OMe)}][\text{ClO}_4]_2$ confirming that no reaction has taken place.

## DISCUSSION

The immediate point of interest is the presence of a different stoicheiometry for the reaction of the hydroxylamine complex compared with that of the free molecule. It is reasonable to postulate an initial *O*-nitrosation to give a Co–$\text{NH}_2\text{ONO}$ species with complications arising at a later stage in the reaction compared to that of hydroxylamine. The failure of the *O*-methylhydroxylamine complex to react is in accord with an initial *O*-nitrosation reaction for the hydroxylamine complex. Rate equation (1) is most readily explained in terms of a rate-determining attack of the nitrite acidium ion $[\text{H}_2\text{NO}_2]^+$ or more probably in terms of current views the nitrosyl ion $[\text{NO}]^+$ on the oxygen atom of the co-ordinated hydroxylamine. Third-order rate constants for the nitrosation of Co–$\text{NH}_2\text{OH}$ and $[\text{NH}_3\text{OH}]^+$ at 34.9 °C are 0.30 and 4.41 dm$^6$ mol$^{-2}$ s$^{-1}$, *i.e.* the co-ordinated hydroxylamine is *ca.* 10% as reactive as $[\text{NH}_3\text{OH}]^+$, which is not unreasonable. There seems no reason therefore to invoke a rate-determining rearrangement of the nitroso-species.

The incursion of the new rate law at lower acidities does not appear to be associated with a change in stoicheiometry. Rate law (2) can be written in a number of ways (3)—(5). Rate law (3) involves the attack of the nitrosating agent involved in (1) on a doubly

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[7] B. C. Challis, L. F. Larkworthy, and J. H. Ridd, *J. Chem. Soc.*, 1962, 5203.

[8] M. N. Hughes, E. D. Phillips, G. Stedman, and P. A. E. Whincup, *J. Chem. Soc.* (*A*), 1969, 1148.

deprotonated hydroxylamine complex, *i.e.* probably on the co-ordinated species $[\mathrm{NHO}]^{2-}$, which would be very susceptible to electrophilic attack. This path would also be favoured because direct *N*-nitrosation could also take place. The reactive form of the complex would, however, be present at very low concentrations. The p$K_1$ value for $NH_2OH$ has been determined [9] to be 13.7, while the p$K_2$ value for ionisation of the nitrogen proton will be higher than this. On the other hand, co-ordination to the doubly charged cobalt(III) centre will result in an appreciable decrease in the p$K$ values. A decrease in p$K$ of between 4 and 6 seems reasonable. It is possible that the value of p$K_2$ for the complex could be in the range 12—16. A value of 14 implies that at $[\mathrm{H}^+] = 10^{-2}$ mol dm$^{-3}$ the fraction of complex present as the doubly deprotonated species will be *ca.* $10^{-10}$ This must cast some doubt on the validity of rate law (3).

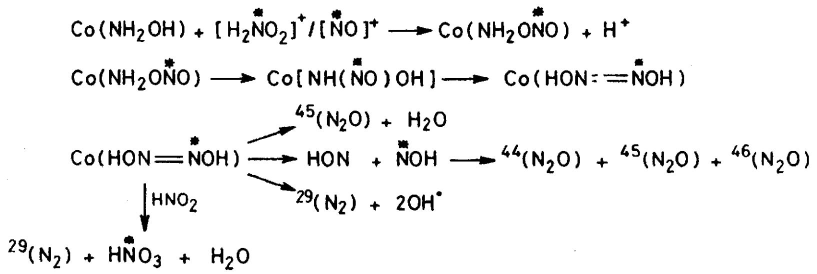
$$\text{Rate} \propto [\mathrm{H}^+][\mathrm{HNO_2}][\text{complex} - 2\mathrm{H}^+] \qquad (3)$$

$$\text{Rate} \propto [\mathrm{HNO_2}][\text{complex}-\mathrm{NH_2O^-}] \qquad (4)$$

$$\text{Rate} \propto [\mathrm{NO_2^-}][\text{complex}-\mathrm{NH_2OH}] \qquad (5)$$

Rate law (4) postulates reaction between molecular nitrous acid and a singly deprotonated complex. Such reactions of $HNO_2$ have not been observed in the past, but may still be a more feasible proposition than (3) in the present case. Rate law (5) involves attack of nitrite on the complex. This would lead to the formation of a nitro-complex, which is not observed in practice. Rate law (5) is therefore excluded.

By analogy with earlier work on hydroxylamine it seems that the initial nitrosation is followed by rearrangement to give a hyponitrite species. In view of the production of nitrogen in the present reaction it is noteworthy that hyponitrite can react [10,11] with $HNO_2$ to give nitrate and nitrogen, and that $HNO_2$ can catalyse a disproportionation of hyponitrous acid, giving nitrogen. This reaction between $HNO_2$ and $H_2N_2O_2$ is not significant in the hydroxylamine–nitrous acid reaction in view of the short lifetime of the intermediate hyponitrous acid, which is attributed to the formation of the *cis* isomer. However, it is possible that in the reaction of the hydroxylamine complex with $HNO_2$ either the hyponitrite species is stabilised on the cobalt(III) centre or the *trans* isomer is formed, so allowing further reaction with nitrous acid to give nitrogen.



In the above scheme the ligands on the cobalt(III) complex are not shown, while labelled nitrogen atoms are indicated by an asterisk. The formation of $N_2O$ of mass numbers 44 and 46 requires cleavage of the hyponitrite species into nitryl fragments, but the present scheme does not appear to account quantitatively for the relative amounts of these products.

No attempt has been made to interpret the kinetic behaviour at acidities corresponding to the minimum reaction rates. A rate that is zero order in $[\mathrm{HNO_2}]$ could result from rate-determining loss of hydroxylamine from the complex, followed by reaction with nitrous acid in a subsequent fast step. This scheme is eliminated by the known stability of the complex under the present conditions and the production of nitrogen.

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[9] M. N. Hughes, H. G. Nicklin, and K. Shrimanker, *J. Chem. Soc.* (*A*). 1971, 3485.

[10] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 4230.

[11] J. R. Buchholz and R. E. Powell, *J. Amer. Chem. Soc.*, 1965, **87**, 2350.