

Nitrosylmolybdenum(III) Moiety: the environmental Catalyser in the Course of Chemical Evolution

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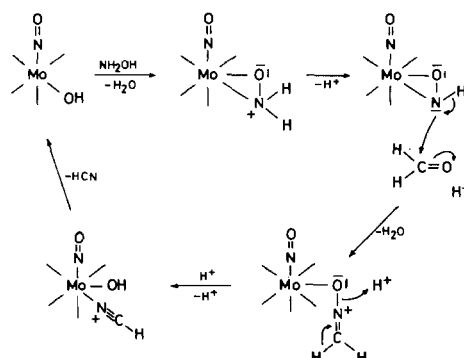
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Egami *et al.* [1, 2] have recently suggested the role of molybdate(VI) as environmental catalyser in the synthesis of biomolecules in prebiotic condition in primeval sea. The proposed mechanism for such reactions was based on Strecker's synthesis with hydrocyanic acid as precursor intermediate. However, though they observed that molybdate(VI) has specific catalytic activity, the role of this in such processes has not been elucidated. Moreover, the essential formation of hydrocyanic acid was assumed from successive dehydration processes in aqueous medium which demands an explanation. We report here that we have now characterized the molybdenum species as nitrosylmolybdenum(III) moiety which acts as catalyst in such processes.

The mechanism by which $\{\text{MoNO}\}^4$ † moiety catalyses the formation of hydrocyanic acid by the interaction between formaldehyde and hydroxylamine in aqueous medium (pH = 5.5) was studied in the following way. First, it has been observed that formaldehyde has neither redox nor any complex chemistry with sodium molybdate(VI) in aqueous medium. Next, the interaction between a fixed amount of 0.15 M molybdate(VI) with a varied range of 0.15 M hydroxylamine were experimented in the same medium with time and temperature variations. The catalytic activity of these reaction mixtures was monitored by their ability to generate hydrocyanic acid on reacting with 0.015 M formaldehyde employing the test of hydrocyanic acid by the method described by Schilt [3]. The results were set out in Table I. We interpret these data in the following way. The interaction between molybdate(VI) and hydroxylamine upto the stoichiometric ratio 1:2 ‡

respectively involved in generating $\{\text{MoNO}\}^4$ moiety leaving no free hydroxylamine to interact with formaldehyde to generate hydrocyanic acid. This is in accordance with the known chemistry of molybdate(VI)–hydroxylamine interaction as observed by us [4, 5] and by others [6]. The catalytic activity with $[\text{MoNOCl}_5]^{2-}$ and NH_2OH substantiate this (see Table I). The lack of catalytic activity of tungstate(VI) supports this view [1] as no nitrosyltungsten chemistry is known by the interaction of tungstate(VI) and hydroxylamine under similar conditions. However, chromate(VI) also lacks the specific activity [1] and it can readily form $\{\text{CrNO}\}^5$ moiety [4] suggesting something more about the $\{\text{MoNO}\}^4$ moiety. This can be viewed in the following way. The $\{\text{MoNO}\}^4$ moiety is able to expand its octahedral coordination [7] to seven coordination even by chelation of hydroxylamido (–I and –II) group resulted from the stepwise deprotonation of hydroxylamine [6]. We have observed in the course of reaction $\{\text{MoNO}\}^4 + \text{NH}_2\text{OH} \rightarrow \{\text{Mo}(\text{NO})_2\}^6$ [5] that a seven coordinated $[\text{Mo}(\text{NO})(\text{NH}_2\text{O})\text{X}_4]^{2-}$ (X = Cl^- , CNS^-) is the first intermediate product, which presumably deprotonated to give the dinitrosylmolybdenum(II) moiety. This dinitrosylation step can be completely stopped by using excess of any aldehyde or ketone. The use of acetaldehyde resulted in the formation of acetonitrile whereas the use of acetone gave only the oxime monitoring the products by i.r. spectroscopy. Thus, in order to react with formaldehyde the hydroxylamine first gets chelated with the $\{\text{MoNO}\}^4$ moiety to give a seven coordinated complex with $\{\text{Mo}(\text{NO})(\text{NH}_2\text{O})\}^4$ group (more stable than $\{\text{MoNO}\}^4$ moiety as it acquires 18 electron configuration). Hence, we conclude the mechanistic view of the continuous hydrocyanic acid generating cycle in the following way:



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† $\{\text{MoNO}\}^4$ notation takes the nitrosyl group as NO^+ (strong Mo–N–O interaction) where 4 stands for a d^4 system; see also, S. Sarkar and A. Mueller, *Angew. Chem.*, 89, 479 (1977); *Angew. Chem. Int. Ed. Eng.*, 16, 468 (1977).

‡ The ratio 1:3 is more plausible as with increase in time and temperature no free hydroxylamine remains in the reaction mixture (see Table I).

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TABLE I. Catalytic Activity of MoO_4^{2-} or $\{\text{MoNO}\}^4$ Moiety to generate HCN with SCHO in the Presence of Varying Amounts of Hydroxylamine at Different Conditions in 0.5 M NaCl Aqueous medium (pH = 5.5).

Ratio between MoO_4^{2-} † (a) or $[\text{MoNOCl}_5]^{2-}$ (b) (ref. 7) with hydroxylamine used (Test Solution)	Temp. of the medium (°C)	Time of addition ^φ of HCHO into the test solution (in min.)	Result ^c HCN test
1(a): 1	20	0	-ve
		90	-ve
	60	0	-ve
		90	-ve
1(a): 2	20	0	-ve
		90	-ve
	60	0	-ve
		90	-ve
1(a): 3	20	0	trace
		90	+ve
	60	0	trace
		90	-ve
1(a): 5	20	0	+ve
		90	+ve
	60	0	+ve
		90	+ve
1(b): 1	20	0	+ve
		90	+ve
	60	0	+ve
		90	+ve
1(a): 0	20	0	-ve
		90	-ve

† 363 mg $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 0.5 M NaCl aqueous solution and 104.20 mg $\text{NH}_2\text{OH} \cdot \text{HCl}$ was added into it. The pH of the solution was adjusted to 5.5 by adding KOH solution in 0.5 M NaCl and the final volume was made to 10 ml by adding 0.5 M NaCl solution to give a concentration of MoO_4^{2-} (0.15 M) and NH_2OH (0.15 M) in 1(a): 1 ratio. For others, $\text{NH}_2\text{OH} \cdot \text{HCl}$ was added: 208.4 mg for 1(a): 2; 312.6 mg for 1(a): 3 and 521.0 mg for 1(a): 5 in alike condition. For the less soluble $\text{Cs}_2[\text{MoNOCl}_5]$, 57 mg of this was taken against 7.0 mg of $\text{NH}_2\text{OH} \cdot \text{HCl}$ to get 1(b): 1 in 0.01 M: 0.01 M concentration ratio.

^φ A ten-fold dilute solution of formaldehyde, e.g., 0.015 M for (a) and 0.001 M for (b) were used in equal volume to the test solution. Experiments were carried out in N_2 atmosphere, however, no appreciable change in the results was noticed in aerobic condition.

^c Trace meant a faint colour in CHCl_3 alike to a blank run with NH_2OH and HCHO employing the method, ref. 3.

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