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Kinetic Identification of the Reactive Cerium(IV) Species in the Oxidation of Methyliminodiacetic Acid (MIDA) in Acidic Sulfate Media*

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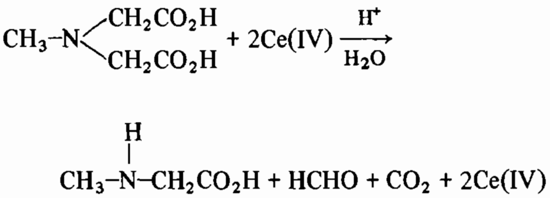
Detailed kinetic analysis of oxidations with Ce(IV) in sulfuric acid media has always been hampered by the difficulty of controlling the concentrations of the various ionic species of the metal ion, *viz.* $CeSO_4^+$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$. Recently, we proposed the system $HClO_4$–Na_2SO_4–$NaClO_4$ as an ideal acidic sulfate medium where $[H^+]$ can be varied independently of the sulfate concentration while maintaining a defined and constant ionic strength, and where the concentrations of the various Ce(IV) sulfato species can be controlled and readily computed [1]. Such a system allows us to pinpoint the kinetically significant species of Ce(IV) in its reactions with reducing ligands [2].

Our previous investigations with polyaminocarboxylic acids as reducing ligands have been of an exploratory nature. The multiplicity of products and the variable stoichiometry observed in the degradation of EDTA [3], prompted us to seek a simpler compound for the present study. We found the simplest amino acid, glycine, to be resistant to oxidation by Ce(IV) whereas iminodiacetic acid is reported to be very slowly oxidized [4]. Methyliminodiacetic acid, MIDA, was chosen for this study because we found it to be the simplest amino acid which is susceptible to oxidative decarboxylation by Ce(IV) at a reasonable rate.

At 25 °C, two equivalents of Ce(IV) are reduced rapidly by reaction with MIDA. The products were identified to be N-methylglycine (sarcosine), formaldehyde, CO_2 and Ce(III). In the presence of excess Ce(IV) formaldehyde yields formic acid whereas sarcosine resists oxidation.



$$CH_3{-}N(CH_2CO_2H)_2 + 2Ce(IV) \xrightarrow[H_2O]{H^+} CH_3{-}NH{-}CH_2CO_2H + HCHO + CO_2 + 2Ce(IV)$$

The reaction rates were followed by monitoring the consumption of Ce(IV) at 300–316 nm in a stopped-flow apparatus as described previously [2]. In the presence of a 20-fold excess MIDA the rate data in either acidic perchlorate or acidic sulfate media fitted the rate equation

$$-d[Ce(IV)]/dt = k_{obs}[Ce(IV)]$$

where k_{obs} is the pseudo first-order rate constant and includes the concentration of MIDA. The rate data (Table) show the effect of addition of Na_2SO_4 in decreasing k_{obs} at constant $[H^+]$ and fixed ionic strength, $\mu = 2$. Such a decrease is to be expected and actually reflects increasing sulfato complexation and the resultant increasing competition between the sulfate groups and the substrate's ligands for positions in the coordination sphere around Ce(IV). In $HClO_4$ the weakly coordinating ClO_4^- surrenders readily to the MIDA ligands and we observe a shift in the Ce(IV) absorbance from 295 nm to 310 nm, which is probably due to complex formation, when MIDA is

TABLE. Observed First-Order Rate Constants and the Percent Distribution of Ce(IV) Species in 0.50 *M* $HClO_4$ at Different Concentrations of SO_4^{2-} and at Ionic Strength, $\mu = 2$ ($NaClO_4$).

$[SO_4^{2-}]$, *M* × 10^4	k_{obs}, sec^{-1}	$CeOH^{3+}$	$Ce(OH)_2^{2+}$	Ce^{4+}	$CeSO_4^{2+}$	$Ce(SO_4)_2$	$Ce(SO_4)_3^{2-}$
0	0.26	76.0	18.0	6.0	–	–	–
5	0.175	16.77	4.02	1.31	66.32	11.38	0.19
7	0.174	12.17	2.92	0.95	67.49	16.18	0.39
40	0.06	1.21	0.29	0.09	38.43	52.73	7.23
70	0.049	0.45	0.11	0.04	24.99	60.00	14.40
100	0.033	0.22	0.05	0.02	17.78	60.99	20.92
200	0.016	0.01	0.01	0.003	7.95	54.55	37.42

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injected into a Ce(IV)/$HClO_4$ solution [5]. In the presence of sulfate, Ce(IV) absorbs strongly at 316 nm and we have not been able to detect complex formation in such media.

Inspection of the data in the Table suggests that $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ are relatively unreactive. On the other hand, the changes in $[CeSO_4^{2+}]$ closely parallel the changes in k_{obs}. Regression analysis of the data further indicates that neither $CeOH^{3+}$ nor $Ce(OH)_2^{2+}$ has a significant effect on the overall reaction rate. However, the uncomplexed Ce^{4+} appears to be ~30 times as reactive as $CeSO_4^{2+}$ and, at constant [MIDA], the data best fit the expression

$$-d[Ce(IV)]/dt = 5.28[Ce^{4+}] + 0.16[CeSO_4^{2+}]$$

We conclude then that of all the species whose concentrations are calculable by known equilibrium constants [6], Ce^{4+} and $CeSO_4^{2+}$ seems to be the kinetically significant participants in the oxidative pathway of MIDA by Ce(IV) in acidic sulfate media.

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References

1 S. B. Hanna, R. R. Kessler, A. Merbach and S. Ruzicka, *J. Chem. Educ., 53,* 524 (1976).

2 S. B. Hanna and S. A. Sarac, *J. Org. Chem., 42,* 2063 (1977).

3 S. B. Hanna, W. R. Carroll, S. Attiga and W. H. Webb, *Z. Naturforsch. B, 30,* 409 (1975).

4 G. N. Rao, *Ind. J. Chem., 8,* 328 (1970).

5 The details of the kinetics of complex formation and eventual reduction of Ce(IV) by MIDA in $HClO_4$ media are the subject of a future paper.

6 For values of equilibrium constants used in the computations see ref. 1.