

Radiation Chemical Studies of Nickel-Glycine. Hydrogen Abstraction by OH Radicals and Oxidation by Br_2^- ¹

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(Received: December 2, 1980)

Reactions of hydroxyl radicals with Ni(II)-glycine complexes were studied by pulse radiolysis and by product analysis. Radiolytic degradation of the complexes in N_2O -saturated solutions leads to the formation of carbonyl compounds. The nature and the yield of these products indicate that the transient formed by reaction of OH with the complex undergoes disproportionation. The optical absorption spectrum of this transient exhibits a maximum below 250 nm, which is similar to that observed with glycine alone. The reaction of Br_2^- with the complex is found to be too slow to be observed by pulse radiolysis. However, the reaction occurs in steady-state radiolysis and yields products different from those observed with OH. Specifically, the yield of formaldehyde is appreciably higher in the presence of Br^- . It is concluded that Br_2^- oxidizes the metal center of the Ni(II)-glycine complex to Ni(III), whereas OH reacts by hydrogen abstraction to form Ni(II)-coordinated glycine radical.

Introduction

A study of the reaction of OH radicals with Ni(II) aminocarboxylates is interesting because of the two possible modes of reaction. If the reaction occurs at the ligand, the result is a metal-coordinated radical, while, if the attack takes place at the metal center, the result may be a Ni(III) state. Earlier findings are, however, controversial. There are reports³⁻⁵ which stress the formation of Ni(III), whereas others⁶⁻⁸ favor the formation of a radical intermediate. In our recent investigation⁸ with the Ni(II) complexes of iminodiacetic acid, we have observed that a metal-coordinated radical, rather than Ni(III), is formed as a result of the reaction of OH with the complex. Attempts have, therefore, been made here to reinvestigate the Ni(II) complexes of the simplest amino acid, glycine, which were studied earlier³ only by pulse radiolysis but not supported by product analysis. In the present study, the reactions of both OH and Br_2^- were investigated and compared. While Br_2^- oxidizes the metal center, OH probably reacts at the ligand rather than at the metal center of the nickel complexes of glycine.

Experimental Section

Materials. All chemicals used in this investigation were of analytical reagent grade. Water was purified by a Millipore Milli-Q system. Nickel-glycine complexes (and their mixtures with the uncomplexed components) were prepared by mixing NiSO_4 and glycine in certain mole ratios. The pH was adjusted by using HClO_4 or NaOH .

Analysis. Glyoxalic acid and formaldehyde were determined with the use of 2,4-dinitrophenylhydrazine reagent. In the case of the former, the hydrazones were

TABLE I: Product Yields in the γ Radiolysis of Ni-Glycine Complexes in N_2O -Saturated Solution

[Ni ^{II}], M	[glycine], M	conditions	$G(\text{CHOCO}_2\text{H})$	$G(\text{CH}_2\text{O})$
1×10^{-2}	1×10^{-2}	pH 7.3	2.2	0.2
1×10^{-2}	1×10^{-2}	pH 7.3, 0.7 M Br^-	1.4	0.9
1×10^{-2}	3×10^{-2}	pH 7.0	1.5	0.4
1×10^{-2}	3×10^{-2}	pH 7.0, 0.8 M Br^-	0.8	3.8
1×10^{-2}	3×10^{-2}	pH 8.1	1.8	0.4
1×10^{-2}	3×10^{-2}	pH 8.1, 0.8 M Br^-	1.6	1.2
1×10^{-2}	3×10^{-2}	pH 9.8	1.9	0.2
1×10^{-2}	3×10^{-2}	pH 9.8, 0.7 M Br^-	1.6	0.4

extracted⁹ into ethyl acetate from which the hydrazone of glyoxalic acid was back-extracted into 10% aqueous sodium carbonate. The aqueous extract was further treated with NaOH , and the absorbance of the resulting solution was measured at 450 nm. For formaldehyde, the hydrazones were extracted in CCl_4 and the optical density of the organic layer was measured at 380 nm. Correction was, however, made for the absorbance due to glyoxalic acid. Calibrations were carried out with similar solutions containing known concentrations of formaldehyde and/or glyoxalic acid.

Irradiation. γ irradiations of samples were carried out for 5-30 min in a ^{60}Co source, the dose rate of which was 3.1×10^{17} eV g^{-1} min^{-1} as determined with the use of the Fricke dosimeter taking $G(\text{Fe}^{3+}) = 15.6$. The pulse radiolysis experiments were carried out with the computer-controlled apparatus described previously.¹⁰

Results and Discussion

Table I shows that the radiolytic products from N_2O -saturated solutions containing nickel sulfate and glycine in different molar ratios and under different pH values constitute mainly glyoxalic acid and a little formaldehyde. It is interesting to note that the overall yields of carbonyl components approach $\frac{1}{2} G_{\text{OH}} (\approx 3)$. This can be explained if the transient formed initially through reaction of OH

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2194 from the Notre Dame Radiation Laboratory.

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(3) Lati, J.; Meyerstein, D. *Inorg. Chem.* 1972, 11, 2397.

(4) Lati, J.; Meyerstein, D. *Int. J. Radiat. Phys. Chem.* 1975, 7, 611.

(5) Lati, J.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* 1978, 1105.

(6) Bhattacharyya, S. N.; Kundu, K. P. *Radiat. Res.* 1972, 51, 45.

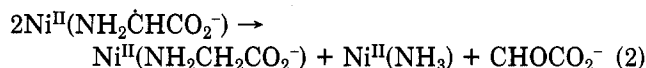
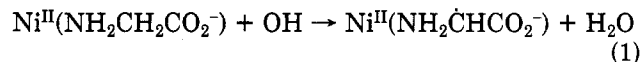
(7) Srisankar, E. V.; Bhattacharyya, S. N. *J. Chem. Soc., Dalton Trans.* 1980, 675.

(8) Bhattacharyya, S. N.; Saha, N. C.; Neta, P. *J. Phys. Chem.* 1981, 85, 300.

(9) Friedemann, T. E.; Haugen, G. E. *J. Biol. Chem.* 1943, 147, 415.

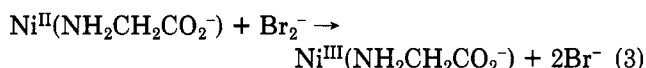
(10) Patterson, L. K.; Lillie, J. *Int. J. Radiat. Phys. Chem.* 1974, 6, 129.

disproportionates. If the transient is a carbon-centered radical, the disproportionation leads mainly to glyoxalic acid.

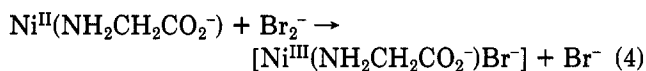


On the other hand, if the transient is Ni(III)-glycine, it is likely to undergo an intramolecular electron transfer resulting in oxidation of the carboxylate group and followed by decarboxylation to yield mainly formaldehyde. This route appears to be unimportant in the reaction of OH with Ni-glycine.

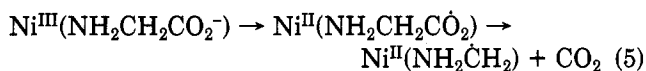
In order to confirm that oxidation to Ni(III) leads to production of CH_2O rather than CHOCO_2H , Ni-glycine was reacted with Br_2^- instead of OH. Br_2^- has earlier been found to oxidize Ni^{II} to Ni^{III} in Ni^{II}-IDA (iminodiacetate) complexes and to yield formaldehyde.⁸ The rate constants for the reaction of 1:1 and 1:2 complexes of Ni-IDA with Br_2^- were found to be 1.7×10^6 and $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively, as determined from pulse radiolytic observations of the decay of Br_2^- absorption at 360 nm. A similar study with Ni-Gly showed that the reaction in this case is too slow to be followed by pulse radiolysis, probably $<10^5 \text{ M}^{-1} \text{ s}^{-1}$. However, the reaction may take place under the low-dose, steady-state irradiation, where the lifetime of Br_2^- is much longer. The product yields, given also in Table I, are clearly different from those obtained upon reaction with OH. It is evident from Table I that, when Br^- is present during radiolysis, the yield of glyoxalic acid decreases but the yield of formaldehyde increases. This increased yield of formaldehyde is associated with the oxidation of the metal center by Br_2^- , either by outer-sphere electron transfer (eq 3) or by the intermediate



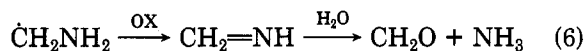
formation of a bromo complex (eq 4). Formaldehyde is



then produced by decarboxylation (eq 5), followed by



disproportionation or oxidation of the radical, and hydrolysis, as discussed previously for the Ni-IDA⁸ or the Ag-glycine¹¹ systems (eq 6).



The highest yield of formaldehyde is obtained at pH 7, even though at this pH only part of the Ni^{II} and glycine are complexed. Br_2^- is not likely to react with either of these components,¹² but it probably reacts with the complex. The overall yield of carbonyl compounds reaches $G = 4.6$, considerably higher than $1/2G(\text{Br}_2^-)$, which is expected to be $G \approx 3.5-3.8$. This indicates that the radicals are partly oxidized and partly disproportionate. Slow

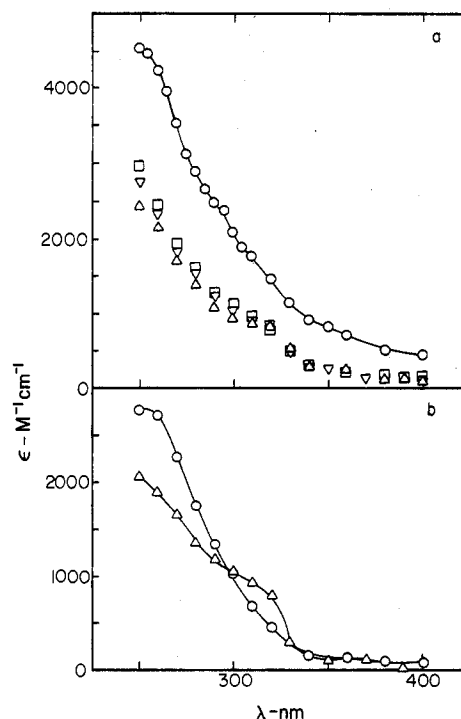
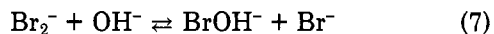


Figure 1. Transient absorption spectra observed in the pulse radiolysis of (a) Ni-glycine complexes and (b) glycine, in N_2O -saturated aqueous solutions. Part a: (O) $2 \times 10^{-3} \text{ M NiSO}_4 + 6 \times 10^{-3} \text{ M glycine}$, pH 10, recorded $5 \mu\text{s}$ after the pulse; (□) $2 \times 10^{-3} \text{ M NiSO}_4 + 6 \times 10^{-3} \text{ M glycine}$, pH 6.6, $11 \mu\text{s}$ after the pulse; (∇) $2 \times 10^{-3} \text{ M NiSO}_4 + 4 \times 10^{-3} \text{ M glycine}$, pH 6.6, $12 \mu\text{s}$ after the pulse; (Δ) $2 \times 10^{-3} \text{ M NiSO}_4 + 2 \times 10^{-3} \text{ M glycine}$, pH 6.6, $14 \mu\text{s}$ after the pulse. Part b: (O) $6 \times 10^{-3} \text{ M glycine}$, pH 10, $5 \mu\text{s}$ after the pulse; (Δ) $4 \times 10^{-3} \text{ M glycine}$, pH 6.6, $14 \mu\text{s}$ after the pulse. In all cases the radiation pulses used supplied energy to produce 3–5 μM of total concentration. The extinction coefficients were determined by using thiocyanate dosimetry and assuming the production of one species with a yield of $G = 6$. In those cases where a mixture of radicals is produced, the ϵ scale should be used only as a relative absorbance scale.

oxidation by Ni^{II} within the metal-coordinated radical may account for this finding.

Increasing the pH from 7 to 8.1 and 9.8 causes a dramatic decrease in $G(\text{CH}_2\text{O})$, accompanied by an increase in $G(\text{CHOCO}_2\text{H})$ and a decrease in the overall yield (Table I). These results probably reflect the low rate of reaction of Br_2^- with Ni-gly and the onset of competing processes dependent on OH^- , e.g., reactions 7 and 8 or other routes of back-reaction leading to OH^- .¹³



It is concluded from the above findings that, while Br_2^- oxidizes $\text{Ni}^{\text{II}}\text{-Gly}$ to $\text{Ni}^{\text{III}}\text{-Gly}$, the attack of OH radicals is mainly on the ligand. This is in disagreement with a previous conclusion³ based on kinetic spectrophotometric studies. It was, therefore, decided to carry out pulse radiolysis experiments with this system. The transient absorption spectra recorded with N_2O -saturated solutions of Ni^{II} + glycine and of glycine alone are shown in Figure 1. All of the spectra have maxima at or below 250 nm. Special attention was given to the problem of scattered light in the spectrophotometric measurements, since this might result in incorrect absorption peaks. The spectra were recorded with the optical system optimized to give $<10\%$ scattered light at 250 nm and $<1\%$ at 260 nm, and

(11) Kumar, A.; Neta, P. *J. Am. Chem. Soc.* 1980, 102, 7284.

(12) Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1977, No. 65.

(13) Mamou, A.; Rabani, J.; Behar, D. *J. Phys. Chem.* 1977, 81, 1447 and references therein.

correction for this measured scattered light was made in all cases. The top spectrum in Figure 1a was recorded with an N₂O-saturated solution containing 2×10^{-3} M Ni^{II} and 6×10^{-3} M glycine at pH 10 and can be assigned to the radical produced by reaction of OH with Ni(gly)₃. The previously reported³ $\lambda_{\max} = 285$ nm measured with an identical solution may have been too high owing to the effect of scattered light. At pH 6.6, where only part of the Ni and glycine are complexed, the spectrum is less intense (Figure 1a, lower experimental points) and approaches that obtained from glycine itself at the same pH (Figure 1b). When the concentration of glycine in the mixture with Ni^{II} is increased, the spectrum of the radicals becomes more intense because of increased complexation.

The rates of formation of the transient absorptions shown in Figure 1 vary widely and depend on the pH and the composition of the solution. Glycine itself reacts with OH with rate constants¹⁴ of $\sim 10^7$ M⁻¹ s⁻¹ at pH 7 and $\sim 2 \times 10^9$ M⁻¹ s⁻¹ at pH >10. Ni(gly)₃ at pH 10 reacts³ slightly faster, $\sim 5 \times 10^9$ M⁻¹ s⁻¹. The rates measured here corroborate these values. The rates of formation measured with solutions containing 2×10^{-3} M Ni^{II} and 2×10^{-3} , 4×10^{-3} , and 6×10^{-3} M glycine at pH 6.6 were found to be

3.0×10^5 , 4.5×10^5 , and 7.0×10^5 s⁻¹, respectively. These values are ~ 10 times higher than the rates expected for glycine alone at the above concentrations, indicating that OH radicals react mostly with the Ni-glycine complexes in these mixtures. The spectra recorded with these solutions (Figure 1a, lower experimental points) can be probably assigned to Ni^{II}(NH₂CHCO₂⁻), while the top spectrum in Figure 1a, which is obtained with Ni(gly)₃ at pH 10, can be assigned to (-O₂CCH₂NH₂)₂Ni^{II}(NH₂CHCO₂⁻). The latter radical thus appears to have a higher extinction coefficient than the former. As mentioned above, an attempt to oxidize these complexes with Br₂⁻ and record the transient spectra in the pulse radiolysis experiment indicated that this reaction is far too slow to be observed directly. However, from the product yields in the steady-state radiolysis discussed above, it is quite certain that the spectra in Figure 1a are assignable to Ni^{II}-coordinated glycine radicals rather than to Ni^{III}-glycine complexes.

In conclusion, Br₂⁻ oxidizes Ni(II)-glycine at the metal center to form Ni(III)-glycine, while OH abstracts hydrogen from the ligand to form Ni(II)-coordinated glycine radical. The latter undergoes disproportionation to yield mainly glyoxalic acid. Ni(III) oxidizes the glycine within the complex and causes its decarboxylation and eventual production of formaldehyde.

(14) Farhatziz; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1977, No. 59.

Relaxation Experiments in Aqueous Solutions of Ionic Micelles. 1. Theory and Experiments on the System H₂O-Sodium Tetradecyl Sulfate-NaClO₄

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In the first part of this paper, we present a consistent theory of the amplitudes and time constants of relaxation experiments in aqueous solutions of ionic micelles, based on a consequent application of the law of mass action. The theory is applicable not only to pure surfactant solutions but also to solutions with an added electrolyte. It is shown that the amplitudes can be calculated without detailed knowledge of the reaction mechanism, which emphasizes that they are independent of the reaction equation. The analysis permits a convenient method to determine some of the relevant equilibrium properties of the proper micelles, as well as their dependence on the intensive variables. In the second part the theory is applied to experimental results on the system H₂O-NaTS (sodium tetradecyl sulfate)-NaClO₄. The parameters obtained from the analysis of the amplitudes and the time constants are in sufficient agreement with each other.

I. Introduction

Relaxation experiments with diluted aqueous micellar solutions yield two processes. The first is a fast one, which is attributed to the rapid redistribution of the proper micelles. This redistribution leads to a change of the mean aggregation number of the proper micelles, whereas their number remains unchanged. The second slower process is attributed to the establishment of the equilibrium by a flux of aggregates through the minimum of the size distribution, which acts as the rate-determining region. During this process both the number and the mean aggregation number of the proper micelles approach their final equilibrium values. Figure 1 shows a schematic

representation of these two processes.¹

The time constants of the two processes have been analyzed by Aniansson and Wall,² whereas the theory of the corresponding amplitudes has been developed by Teubner et al.³ Although these calculations are strictly valid for nonionic systems only, the theory has been mainly compared with experiments on ionic systems, since the detection of the relaxation processes in nonionic systems meets with considerable experimental difficulties, if one

(1) M. Kahlweit and M. Teubner, *Adv. Colloid Interface Sci.*, **13**, 1 (1980).

(2) E. A. G. Aniansson and S. N. Wall, *J. Phys. Chem.*, **78**, 1024 (1974); **79**, 857 (1975).

(3) M. Teubner, S. Diekmann, and M. Kahlweit, *Ber. Bunsenges. Phys. Chem.*, **82**, 1278 (1978).

[†] Part of Ph.D. Thesis, Göttingen, D 7, 1980.