The study has provided additional evidence that metal interactions at O(6) of Guo and related nucleosides can alter the hydrogen-bonding capabilities of the nucleosides and thereby contribute to base mispairing in DNA molecules. The results that indicate enhanced deprotonation of the thionucleosides due to metal complexation are also of interest since studies have shown that selected metal complexes of thiopurines are more active against certain kinds of tumors than the thiopurines alone.[14]

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Registry No. **1** (R = ribose, X = NH_2), 118-00-3; **1** (R = ribose, X = H), 58-63-9; **2**, 85-31-4; **3**, 26001-38-7; $GuoRh^I$, 85798-23-8; $InoRh^I$, 85798-24-9; s^6GuoRh^I, 85735-72-4; s^8GuoRh^I, 85735-73-5; TEA, 121-44-8; EOA, 141-43-5.

Contribution from the Department of Chemistry, Nuclear Research Center "Demokritos", Aghia Paraskevi Attikis, Athens, Greece, and Laboratory of Inorganic Chemistry, University of Athens, Navarinou 13A, Athens, Greece

Reductive Desulfurization of Mercaptoacetic Acid

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Mercaptoacetate in large excess and in the pH range between 3 and 10 forms with V^{III} intensely yellow complexes, in two successive stages, the second of which was followed by stopped-flow methods at pH 3.6 and found to be first order in vanadium(III) and in mercaptoacetate. The activation parameters are $\Delta H^* = 57.4$ kJ mol^{-1} and $\Delta S^* = -0.8$ J mol^{-1} K^{-1}. Under similar conditions V^{II} undergoes also a two-stage complexation reaction but reacts further, giving succinic acid and hydrogen sulfide. This redox reaction is first order in vanadium(II) and in mercaptoacetate and at pH 9.6 has $\Delta H^* = 50.2$ kJ mol^{-1} and $\Delta S^* = -70$ J mol^{-1} K^{-1}. The second-order rate constant correlates with the titration curve of mercaptoacetic acid. The results are compared to analogous results for cysteine and are interpreted on the basis of a two-step chelate ring formation involving the S^- group. The activation of the V^{II} and V^{III} reactions is partly attributed to proton dissociation of the organic moiety and partly to a strain in the ring, which when combined with electron transfer leads to a break of the C–S bond. The V^{II}–mercaptoacetate system can be regarded as an electron-storing device, which can be activated by changing the proton environment.

Introduction

The reductive cleavage of the carbon–halogen bond has been investigated by many authors.[1] Most of the work was done with Cr^{2+} (aq) as the reductant. The examples of using other reductive metal ions are few.[1] Few also are the examples of breaking other carbon single bonds. Among them one could mention the presumed breaking of the carbon to nitrogen bond in the Cu^I-induced decomposition of diazonium salts[2] and the breaking of the carbon to metal bonds in transalkylation reactions.[3]

Partial reductive desulfurization of compounds associated with coal or petroleum such as dibenzothiophene can be achieved[4] with use of solvated electrons or electrolysis.

Here we report on the cleavage of the carbon to sulfur bond of mercaptoacetic acid, induced by vanadium(II), and discuss briefly some general biological implications.

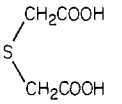
The system is studied in the pH range from ~3 to 10. In this range relatively little is known about mechanisms of redox processes.

The product of the redox process is V^{III} complexed with mercaptoacetate. The same complex is also formed when V^{III} is mixed with mercaptoacetate. The kinetics of this complexation reaction were also investigated.

Experimental Section

Mercaptoacetic acid was purchased from Riedel-de Haen A.G. The main impurities are dithiodiglycolic acid ($HOOCCH_2SSCH_2COOH$), dithioglycolide

and thiodiglycolic acid



Purification was done by fractional distillation under vacuum.[5] The solutions had to be freshly prepared and deaerated.

Determination of the concentration of mercaptoacetic acid (mac[6]) is based on the reaction[5]

$$2HSCH_2COOH + I_2 \rightarrow HOOCCH_2SSCH_2COOH + 2HI$$

Iodine is produced from IO_3^- and I^-.

Vanadium(II) was prepared electrolytically on a mercury cathode.[7] All experiments were performed under an inert atmosphere.

The kinetics were followed with a stopped-flow apparatus (Applied Photophysics), and spectra were recorded with a Cary 14.

Hydrogen sulfide was trapped in a double trap containing a saturated lead acetate solution, by purging the reaction mixture with argon. The reaction mixture was then acidified and the purging continued until all H_2S was obtained in the form of PbS.

Succinic acid was determined in the products by acidifying and passing the reaction mixture through an ion-exchange resin (Dowex 50W-X2) in order to remove vanadium. Alcohol was then added, and the precipitated sodium chloride was filtered. Then the organic acids were esterified with use of BF_3 solution in ether. The esters were separated by gas chromatography (column Apiezon L on Chromosorb G), and the ester of succinic acid was identified by mass spectroscopy.

† Nuclear Research Center "Demokritos".
‡ University of Athens.

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(2) The so-called Sandmeyer reaction: Sykes P. "A Guidebook to Mechanisms in Organic Chemistry", 5th Ed.; Longmans, Green and Co.: New York, 1981.
(3) (a) Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* **1973**, *95*, 4468. (b) Espenson, J. H.; Sellers, T. D. *Ibid.* **1974**, *96*, 94. (c) Endicott, J. F.; Belakrishnan, K. P.; Wong, C. L. *Ibid.* **1980**, *102*, 5519.
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(7) Vrachnou-Astra, E.; Sakellaridis, P.; Katakis, D. *J. Am. Chem. Soc.* **1970**, *92*, 811.

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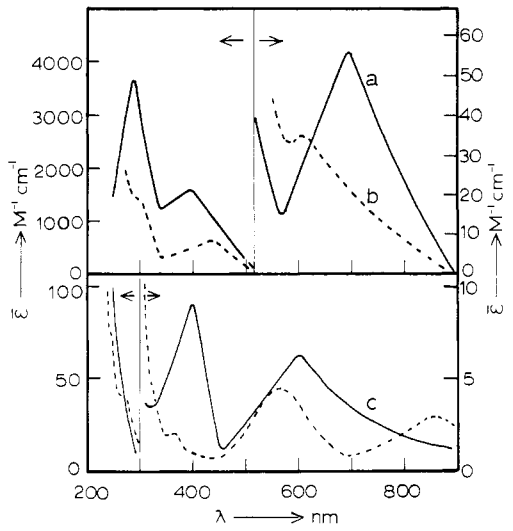

Figure 1. Apparent absorptivities, $\bar{\epsilon}$, of V^{III} + mac (24 °C): (a) pH 9, $[V^{III}]_t = 7 \times 10^{-4}$ M, $[mac]_t = 0.05$ M; (b) pH 4, $[V^{III}]_t = 2.6 \times 10^{-3}$ M, $[mac]_t = 0.1$ M. The spectra can be compared to the spectrum of $V(H_2O)_6^{3+}$ (curve c).

Table I. Spectral Characteristics of the V^{III}–mac System around 400 nm and the Effect of $[V^{III}]_t$ and $[mac]_t$

$10^3[V^{III}]_t$, M	$[mac]_t$, M	pH	λ_{max}, nm	$\bar{\epsilon}_{max}$[a]
0.37	0.02	4.0	430	980
3.70	0.20	4.0	428	640
0.70	0.05	9.1	395	1630
6.50	0.48	9.1	395	1615

[a] Apparent absorptivity obtained by dividing by $[V^{III}]_t$.

pH measurements were made with a Metrohm A.G. Herisau Model 436 potentiograph. Under the conditions of our experiments initial and final values were the same.

Results

V^{III} Complexation. Mercaptoacetate (mac[6]) in large excess and in the pH range between 3 and 10 forms with V^{III} an intensely yellow solution. With a total concentration of mercaptoacetate $[mac]_t = 0.1$ M and $[mac]_t/[V^{III}] > 20$ there is no formation of solid green vanadium(III) hydroxide. In the absence of air and at pH up to ~10 vanadium(III) is not oxidized by mac. The spectra of two typical V^{III}–mac solutions at pH 9 and pH 4 are given in Figure 1. They are significantly different from the spectrum of $V(H_2O)_6^{3+}$ in acid solution, which is also included in this figure for comparison. It should be noted in particular that the two of the three d–d transitions are covered by charge-transfer bands or gain intensity by mixing with such bands.

Characteristic results showing the effect of total V^{III} and mac concentrations are given in Table I, and the effect of pH is shown in Table II. At pH 9.1 the concentrations of V^{III} and mac do not affect (within experimental error) the spectrum, but at lower pH an increase in $[V^{III}]_t$ and $[mac]_t$ results in a decrease of the apparent absorptivity and a small blue shift of λ_{max}. At pH >8 the spectrum is not affected by the ratio $[mac]_t/[V^{III}]_t$—provided that this ratio is kept higher than ~30.

The spectra depend strongly on pH (Figure 1 and Table II). There is a large red shift of the low-energy band at 14.7×10^3 cm^{-1} compared to 17.2×10^3 cm^{-1} of the aquo species and of the V^{III}–cysteine complex.[8] If the second band coincides with the band in the 400-nm region, the values for $V(H_2O)_6^{3+}$, V^{III}–mac (pH 9.1), and V^{III}–cyst are 25.6, 25.3, and 23.5 × 10^3 cm^{-1}, respectively, whereas the value for V^{III}–mac at pH 4 is ~23.2×10^3 cm^{-1}.

Table II. Spectral Characteristics of the V^{III}–mac System around 400 nm and the Effect of pH ([mac] = 0.2 M, $[V^{III}] = 5 \times 10^{-4}$ M)

pH	$\bar{\epsilon}_{max}$	λ_{max}, nm	pH	$\bar{\epsilon}_{max}$	λ_{max}, nm
3.8	960	428	7.4	1450	395
4.5	1140	415	9.2	1700	395
4.8	1170	411	9.5	1750	395
6.5	1190	395			

Table III. Activation Enthalpies and Entropies in the Reactions of V^{II} and V^{III} with mac and Cysteine

reacn	pH	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	linearity, log k/T vs. $1/T$
V^{II} + mac, redox[a]	9.6	50.2 ± 1	−70	0.998
V^{III} + mac, complexation	3.6	57.4 ± 2	−0.8	0.986
V^{II} + cys, complexation	8.2	38.7 ± 5	−122	0.955
V^{II} + cys, redox[b]	8.0	51.2 ± 2	−159	0.993
V^{III} + cys, complexation	8.8	38.0 ± 4	−60	0.950

[a] Production of H_2S. [b] Production of H_2.

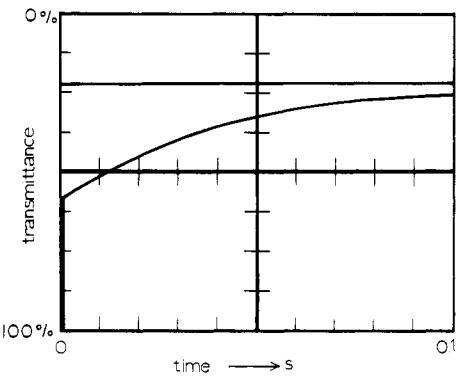

Figure 2. Oscilloscope trace showing the two stages in the reaction between V^{III} and mac, at $[V^{III}]_t = 0.47 \times 10^{-3}$ M, $[mac]_t = 1.3 \times 10^{-2}$ M, temperature 35 °C, pH 3.7, and wavelength 430 nm. The abcissa shows time, 10 ms/div, and the ordinate transmittance.

From Table II we also see that there is a shift in λ_{max} and an increase in $\bar{\epsilon}_{max}$ around 400 nm. At pH ≃ 5 both λ_{max} and $\bar{\epsilon}_{max}$ change abruptly. After pH 5 λ_{max} remains constant, whereas $\bar{\epsilon}_{max}$ remains constant only up to pH 6.5 and then starts increasing again.

Kinetically we observe two stages in the reaction of V^{III} with mac. At high pH values these stages are not resolved and they are too fast to be followed by stopped flow: the transmittance attains its infinity value at zero time. Al lower pH values, however, the two stages are resolvable: one of them appears as a jump at $t = 0$, and the other can be followed with time (Figure 2), provided that the concentrations of the reactants are kept low. Under conditions of excess mac the rate of this second stage at low pH values is pseudo first order, and the observed rate constant depends linearly on [mac]. In a typical plot ($[V^{III}]_t = 5 \times 10^{-4}$ M, 23 °C, pH 3.5) of the log of the pseudo-first-order rate constant obtained in excess mac vs. log [mac], the linearity was 0.98, the least-squares slope was 0.98 ± 0.06, and the second-order rate constant calculated from the slope $k_2 = 361 \pm M^{-1}$ s^{-1}. There is no evidence of contributions from higher order terms.

The log k vs $1/T$ plot gives good linearity (0.99). The activation parameters (at pH 3.6) are $\Delta H^{\ddagger} = 57.4 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -0.8$ J mol^{-1} K^{-1} (Table III). Table III also includes the values for cysteine.[8]

V^{II} Complexation and Redox Reactions. Three kinetically distinguishable stages were observed in the case of V^{II} + mac. The first is too fast to be followed with our stopped-flow

(8) Kalatzis, G.; Konstantatos, J.; Vrachnou-Astra E.; Katakis, D., submitted for publication.

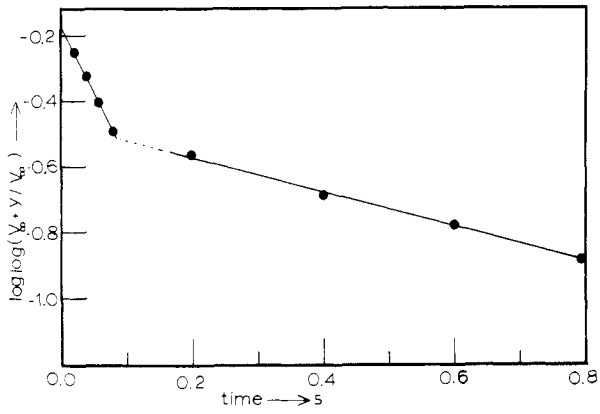

Figure 3. Pseudo-first-order plots showing the last two stages in the reaction of V^{II} with mac, at pH 9.5, temperature 28 °C, wavelength 350 nm, $[V^{II}]_t = 0.55 \times 10^{-3}$ M, and $[mac]_t = 0.14$ M. Observed rate constants are 17 and 1.1 s^{-1}, respectively.

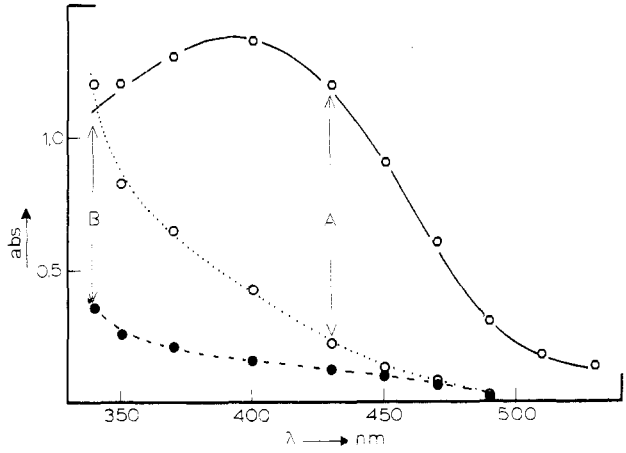

Figure 4. Spectral characteristics of the products in each of the observed three stages in the reaction between V^{II} and mac ($[V^{II}]_t = 5.5 \times 10^{-4}$ M, $[mac]_t = 0.15$ M, pH 9.6, 27 °C): (●) first stage, not followed kinetically, appearing as a jump at $t = 0$ in the stopped-flow photographs; (○) fast but measurable step, at intermediate time; (○) third step (also measurable), representing absorption at $t = \infty$.

instrument. The second is slower and the third even slower. The last two stages are shown in Figure 3.

The spectral characteristics of the products between 340 and 530 nm at pH 9.6 in each of the three stages are shown in Figure 4. At ~430 nm (A in Figure 4) we essentially observe only the third stage (the redox step, vide infra); at ~340 nm (B in Figure 4) we observe only the formation of the intermediate, which at this wavelength has the same (under the conditions given) absorption as the final product.

At pH 4 the spectrum of the intermediate does not differ much from the spectrum of $V(H_2O)_6^{2+}$.

At the end of the second stage (pH 9.6) vanadium is still in the +2 oxidation state. The first two stages, therefore, correspond to complexation. It should be recalled that the substitution reaction of V^{III} at this pH value was too fast to be followed by stopped flow. This increased lability must also be related to base hydrolysis.

The third stage in the V^{II} + mac reaction corresponds to a redox process. The vanadium product obtained is identical with the V^{III}–mac species obtained directly by mixing vanadium(III) and mac solutions. The products from mercaptoacetate are succinic acid and hydrogen sulfide. Vanadium(IV) was not detected. The stoichiometry was determined by measuring V^{II} and H_2S. Typical examples include the following (a) $[mac]_0/[V^{II}]_0 = 10.5$, amount of H_2S formed 0.92 times the amount of V^{II} consumed; (b) $[mac]_0/[V^{II}]_0 = 5.2$, amount of H_2S formed 0.95 times the amount of V^{II} consumed.

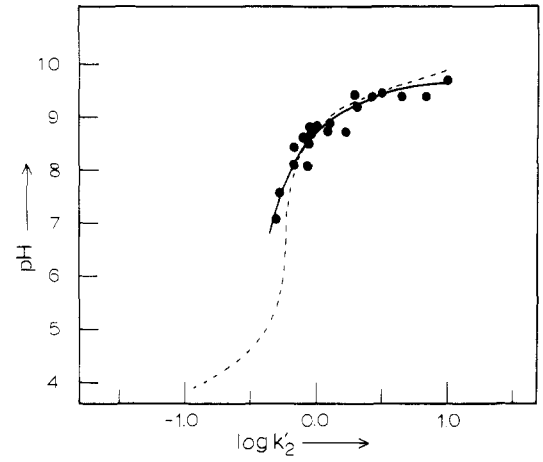

Figure 5. Dependence of the rate constant of the V^{II} + mac redox reaction on pH (solid line) at 24 °C. Included in the figure is also the titration curve of mercaptoacetic acid (dotted line).

Since the only organic product found is succinic acid, the overall reaction is

$$2V^{II} + 2HSCH_2COOH + 2H^+ \rightarrow 2V^{III} + HOOCCH_2CH_2COOH + 2H_2S$$

Over the time period and the temperature range of our experiments mac solutions do not give H_2S. In the experiments with V^{III} there is no H_2S formation. This can also be regarded as a blank.

The rate law is

$$R = k'_2[V^{II}][mac]$$

In a typical plot of the log of the pseudo-first-order rate constants of the redox reaction vs. log [mac] (24 °C, pH 8.7, $[V^{II}]_0 = 5 \times 10^{-4}$ M, mac always in exess) the least-squares slope was 1.10 ± 0.09, which corresponds to $k'_2 = 1.2 \pm 0.1$ M^{-1} s^{-1}.

Activation parameters for the redox step are included in Table III. It is noted that the redox step at high pH values is 20–50 times slower than the preceding substitution equilibrium, which can therefore be considered as having been established.

Figure 5 gives the dependence of the rate constant of the V^{II} + mac redox reaction on pH. At pH values around 4 the reaction is very slow, at least five orders of magnitude slower compared to the reaction at pH 9. With such slow rates interference by even small amounts of impurities becomes significant.

In Figure 5 we include the titration curve of mercaptoacetic acid, for comparison—without corrections for converting activities to concentrations. The correlation between kinetics and the titration curve is remarkable.

Discussion

The absence of higher order terms in the rates seems to indicate either that attachment of the second or of the third ligand does not take place or more likely that the rates for the second or third ligand attachment are fast compared to the rate for the first. This kind of labilization has also been observed in the substitution reactions of Co^{II} and Ni^{II} with α-alanine, α-aminobutyric acid, and cysteine.[9]

Under the conditions of our experiments, any contribution from polynuclear species such as the hydrolytic dimer of V^{III}[10]

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seems also to be kinetically insignificant. This is perhaps partly due to the low concentrations of V^{II} and the large excess of mac. The data in Table I provide further support for this assumption. At high pH there is no dependence of $\bar{\epsilon}_{max}$ and λ_{max} on $[V^{III}]_t$ and $[mac]_t$. At low pH the change is in the opposite direction of what one would have expected if dimerization or polymerization took place, and it could be attributed to incomplete complexation.

Accordingly we confine our attention to the attachment of the first organic ligand to a single metal ion. The fact that the break in the log k_2 vs. pH curve for the redox reaction corresponds to a break in the titration curve (Figure 5) and the kinetic data show a reaction first order in vanadium and in mercaptoacetate seems to indicate that removal of the protons from the COOH and SH groups precedes electron transfer. The pK values for these groups (for the uncoordinated ligand) are 3.58[11a] and 9.78[11a] (10.56[11b]), respectively. Therefore, throughout most of the pH range investigated the carboxyl group is fully dissociated. The break in the log k_2 vs. pH curve in Figure 5 is then probably associated with the sulfhydryl group. In that case, it can be argued that the species undergoing redox reaction contains coordinated S^- and not SH.

The changes in $\bar{\epsilon}_{max}$ and λ_{max} (Table II) at pH $\simeq$5 are perhaps associated with proton dissociation of coordinated water. Between pH $\simeq$5 and pH $\simeq$6.5 the environment around V^{III} seems to remain unchanged, and only above pH $\simeq$6.5 does $\bar{\epsilon}$ start increasing again, presumably because of sulfur coordination and contribution to the $\sim$400-nm peak from charge transfer. The $\bar{\epsilon}_{max}$ values above this pH also follow fairly well the titration curve (Figure 5).

It must be made clear at this point that the pH values are activity values, that the pK value for SH of a coordinated ligand is probably different from that of the free ligand, and that no effort has been made to keep ionic strength constant.

The two steps in the formation of the chelate ring are distinguishable, both spectroscopically and kinetically. We assign the first stage in the complexation of V^{II} and V^{III} with mac (jump at $t = 0$) to the formation of a monodentate species. The reaction for V^{II}, which is probably substitution controlled,[12] is over within the "dead" time ($\sim$5 ms) of our instrument. For V^{III} it is expected to be even faster.[13] The second step in the substitution is the closure of the ring, and in our case it is slower. The situation corresponds to what has been termed as the kinetic chelate effect.[9]

The sequence of events in the case of the V^{II}–mac system can be summarized as follows:

$$V^{II} + HSCH_2COO^- \rightarrow V^{II}\text{—}O\text{—}C(=O)\text{—}CH_2\text{—}SH^* \xrightarrow{+H^+}$$

$$\xrightarrow{+H^+} V^{III} + H_2S + CH_2COO^-\cdot$$

$$2CH_2COO^-\cdot \rightarrow {}^-O_2CCH_2CH_2CO_2^-$$

In the case of V^{III}–mac there is no redox step.

The activation enthalpy for substitution (second stage) on the usually labile V^{III} is unexpectedly high. In fact, this value is slightly larger than the value for the rate-determining step in the redox reaction of V^{II} with mac. It is also noted that the entropy term for the second stage in the V^{III} complexation is close to zero, which is not what one would have expected for chelation. These "anomalies" can partly be attributed to the enthalpies and entropies of the preceding proton release equilibria, which are included in the observed activation. For the carboxyl proton dissociation equilibrium the literature[11] values of $\Delta H°$ are close to zero, for both mercaptoacetic acid and cysteine. There is, however, a sizable negative entropy contribution from this dissociation (−70 and −50 J mol^{-1} K^{-1}, respectively). For the SH group the values of $\Delta H°$ and $\Delta S°$ for mercaptoacetic acid reported in the literature[11] range from 26 to 27 kJ mol^{-1} and 100 to 115 J mol^{-1} K^{-1}, respectively. The corresponding values for cysteine are 34–40 kJ mol^{-1} and −40 to −70 J mol^{-1} K^{-1}. Thus, these thermodyamic parameters seem to account adequately for the apparent activation in the case of cysteine. In that case we can argue[8] that steric factors are unimportant, but with mercaptoacetate, such factors cannot be disregarded. After subtraction of the proton dissociation enthalpies and entropies, there is still considerable activation left. In fact this activation seems, strangely enough, to be of the same order of magnitude for V^{II} and V^{III}. In other words, it seems to be associated with the ligand rather than with the metal ions. The forceful formation of the strong sulfur-to-metal bond presumably introduces considerable strain into the skeleton of the ligand. In fact it is probably this strain, in combination with electron transfer from V^{II}, that eventually leads to the breaking of the C–S bond and formation of hydrogen sulfide and the organic free radical, $\cdot CH_2COOH$-, which subsequently dimerizes to succinic acid. In the case of V^{III} the "shock" from the formation of the M–S bond is not accompanied by electron transfer and its does not lead to a break of the C–S bond.

The spectra are consistent with this picture. They indicate that the field in the V^{III}–mac complex (high pH) is unusually weak and delocalization of the electrons small. This is perhaps because the "bite" is large and the metal to ligand distances are relatively long. In the case of cysteine, where there is no strain, the field is stronger and delocalization more pronounced.

In closing this discussion, we wish to briefly touch upon some aspects of a more general nature and of special interest for biological redox systems. The V^{II}–mac system can be regarded as an electron-storing device, which can remain "passive" for a long time, provided the pH is kept low. An increase in pH, however, activates the system and triggers the redox process. This particular system has of course no direct biological relevance, but we believe that there is nothing unique about it and that similar observations can probably be made with other systems as well—which calls for more metal ion chemistry in pHs around neutral.

Acknowledgment. The authors wish to thank Dr. C. Zioudrou for fruitful discussions, Dr. F. Varveri for her advice on gas chromatographic analytical techniques, and B. Papadopoulos for the mass spectrographic analysis of the products.

Registry No. Mercaptoacetic acid, 68-11-1; vanadium(III), 22541-77-1; vanadium(II), 15121-26-3.

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