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Kinetics and Mechanism of the Oxidation of Thiourea and *N,N'*-Dialkylthioureas by Hydrogen Peroxide

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The oxidation of thiourea and two dialkylthioureas to their respective formamidine disulfide cations by hydrogen peroxide in acid solution has been studied kinetically. The rate law and other data indicate that the reactions proceed via a nucleophilic displacement by sulfur on oxygen. The scope of this mechanism for reaction of nucleophiles with peroxides is discussed.

Introduction

Qualitatively, the oxidation of thiourea and its alkyl derivatives with hydrogen peroxide has been thoroughly studied. In acidic solution, the reaction of thiourea with an excess of hydrogen peroxide yields a mixture of ammonia, sulfur, sulfuric acid, and carbon dioxide,[1,2] whereas in neutral solution thiourea dioxide and water are formed.[3]

$$(NH_2)_2CS + 2H_2O_2 \rightarrow 2H_2O + (NH_2)_2CSO_2 \qquad (1)$$

Marshall[2] was the first to report the isolation of the dibasic salt formamidine disulfide bis(hydrogen chloride) from a mixture of acid, thiourea, and hydrogen peroxide.

$$2(NH_2)_2CS + H_2O_2 + 2H^+ = (NH_2)_2CSSC(NH_2)^{2+} + 2H_2O \qquad (2)$$

Formation of a disulfide salt is consistent with the fact that thiols are readily oxidized to disulfides.[4] In a neutral or weakly acidic medium, the disulfide ion spontaneously decomposes with the precipitation of sulfur.[5] Reactions of the type represented by eq 2 have been used to convert a number of *N*-alkylthioureas to *N,N'*-dialkylated dithioformamides.[6,7] The crystal structure of the formamidine disulfide ion verifies the existence of a discreet S–S single bond with a bond length of 2.04 Å. In addition, the dimensions and planarity of the thiourea groups are virtually unaltered in the disulfide product except for a slight lengthening of the C–S bond.[8]

Product formation is thermodynamically favorable as illustrated by the redox couples listed in Table I. The reduction potentials for the thiourea–formamidine disulfide systems range from −0.42 V to −0.46 V. Combination of these values with the peroxide–water reduction couple of +1.76 V indicates that there are powerful thermodynamic driving forces in these reactions.

Thiourea[9] and its analogue dithiobiuret[10] have been reported to react rapidly with hydrogen peroxide. These reactions were considered "too fast" to be measured; consequently, the rate law and mechanism were unknown. Edwards[11] has estimated that the nucleophilic reactivity of thiourea would place it between I^- and $S_2O_3^{2-}$ on a scale of relative rates toward hydrogen peroxide.

Table I. Electrode Potentials for the Thioureas and Hydrogen Peroxide

Couple	E^0
$(NH_2)_2CSSC(NH_2)_2{}^{2+} + 2e^- \rightleftarrows 2(H_2N)_2CS$	-0.418^a
$(CH_3NH)_2CSSC(NHCH_3)_2{}^{2+} + 2e^- \rightleftarrows 2(CH_3NH)_2CS$	-0.460^b
$(C_2H_5NH)_2CSSC(NHC_2H_5)_2{}^{2+} + 2e^- \rightleftarrows (C_2H_5NH)_2CS$	-0.450^b
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	$+1.76^c$

[a] P. W. Priesler and L. Berger, *J. Am. Chem. Soc.*, 69, 322 (1947). [b] P. W. Priesler, *ibid.*, 71, 2849 (1949). [c] W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, Englewood Cliffs, N.J., 1961.

In the present study we examine the kinetics of the thiourea and *N,N'*-alkylthiourea oxidations by hydrogen peroxide and propose a suitable mechanism.

Experimental Section

Reagents. Reagent grade thiourea (tu) (Aldrich) was recrystallized twice from hot water. *N,N'*-Dimethylthiourea (dmtu) and *N,N'*-diethylthiourea (detu) (Chemical Samples Co.) were technical grade. The yellowish dmtu was recrystallized repeatedly from freshly distilled dioxane until clear white crystals were obtained. The resulting crystals, which were vacuum dried, were exceedingly deliquescent and melted in the range of 60–62 °C. Final IR and NMR spectra matched those listed in the Aldrich Spectral Handbook.

Technical grade detu was recrystallized four times from 20% methanol–water. The resulting crystals, which had been vacuum dried, were clear colorless plates. The melting range of 78–80 °C and the IR and the NMR spectra agreed with those reported in the literature. Hydrogen peroxide (90%, FMC) without added stabilizers and reagent grade perchloric acid (70%, B&A) were used as received.

Product Identification. The dihydrochloride salt of formamidine disulfide (dimer) was prepared using the technique of Preisler and Berger.[9] Recrystallized thiourea (4.8 g) was reacted with 5 mL of 30% hydrogen peroxide in 50 mL of 3 M HCl. After the addition of 200 mL of ethanol and 60 mL of concentrated HCl, white crystals precipitated. They were subsequently filtered, washed, and then dried in a vacuum desiccator. The product decomposed at 168 °C. The IR spectrum of the dimer is virtually identical to that of thiourea although the Raman spectrum shows a strong band at 470 cm^{-1} which is characteristic of sulfur–sulfur stretching. The UV spectrum of thiourea has a maximum of 235 nm which tapers off and then asympotically approaches the solvent baseline near 300 nm. The dimer has a noticeably stronger absorption at 300 nm with the maximum difference occurring at 310 nm, where the combined extinction coefficients of the reactants were less than one and that of the dimer was twenty.

Bis(*N*,*N*′-dimethyl)formamidine disulfide was prepared in the same manner as described above except that crystals did not form immediately after the addition of ethanol and concentrated HCl. After the solution stood in a refrigerator for several days, white crystals finally formed. These white crystals were separated, washed, and dried. The resulting crystals decomposed at 132 °C and had an IR spectrum identical to that of dmtu. A maximum change in extinction coefficient of 31 also occurs at 310 nm.

Previous attempts to prepare bis(*N*,*N*′-diethyl)dithioformamidine bis(hydrogen chloride) or the corresponding bis(hydrogen bromide) were unsuccessful.[6,7] Apparently, the high solubility of the products prevented their isolation. A new approach, which had not been previously reported, was used to prepared the dimeric dibromide crystals after attempts to isolate the dimeric dichloride crystals were unsuccessful.

Recrystallized detu (2.65 g) was dissolved in cold chloroform to which 5 mL of 2 M bromine in chloroform was added. The reddish-brown color of the bromine gradually disappeared with total loss of color after 5 min. To this solution excess CCl_4 was added and a viscous oil dropped out of solution. This oil was separated and placed in a vacuum desiccator. After pumping for approximately 30 min, the oily product changed suddently into yellow crystals. Pumping was continued overnight. The resulting crystals were extremely deliquescent and consequently a reliable melting point was unobtainable. The IR, NMR, and UV spectra had the same basic characteristics as detu except for slight shifts. Conductivity measurements verified that the product was ionic. The elemental analysis was consistent with the following formulation:

$$C_{10}H_{24}N_4S_2Br_2\cdot{}^1/{}_2CCl_4$$

	% N	% H	% C
Calcd	11.03	4.82	25.15
Found	11.10	5.13	25.30

Procedures. Preliminary UV spectra were recorded on a Cary 15 while the final spectra used to determine extinction coefficients of reactants and products were obtained from a Hitachi Perkin-Elmer 139.

Kinetic determinations were made with a Durrum-Gibson D-110 stopped flow spectrophotometer which was linked directly to a Hewlett-Packard 1207A oscilloscope. Permanent records of the oscilloscope output were recorded on Polaroid film with a Hewlett-Packard 198A detachable oscilloscope camera. Temperature was maintained within 0.02 °C using a combination of Haake NBS constant temperature circulator with an added heat exchanger for operation below ambient temperature and a Haake E52 immersion circulator. Fresh solutions were prepared for each kinetic determination with triply distilled water which had been degassed by a common vacuum line technique.

Treatment of Data. Data from each kinetic run were obtained in the form of a Polaroid photograph of an oscilloscope trace. The photographs were analyzed using a Hewlett-Packard 9107A magnetic digitizing board with a resolution of 0.01 in. which was interfaced with a Hewlett-Packard 9100B programmable calculator and a 9101A extended memory. A program was written, assuming pseudo-first-order conditions were observed, that allows the distance proportional to ln $(A_\infty - A_t)$ to be measured and multiplied by the appropriate calibration parameters for the vertical axis, which were entered into the program before execution, and those results to be paired with the corresponding time value from the horizontal axis. The ln $(A_\infty - A_t)$ and time values for each data point selected were processed through a linear regression subroutine. The values of ln $(A_\infty - A_t)$, time, slope, intercept, and correlation coefficient were printed as output. To reduce the effect of random errors, a minimum of three photographs was taken of three different traces representing the same reaction conditions. The final result of any set of conditions was the average of the data represented by these photographs. To check the validity of the pseudo-first-order treatment, graphs were obtained simultaneously from a HP(X–Y) plotter with the best straight line drawn through the data points. Due to the volume of data processed, plots were obtained only for an initial sequence of runs under different conditions. Included in the calculator program was a subroutine designed to correct for any random vertical or horizontal positioning of the photograph on the digitizer relative to an internal set of coordinates.

Results

Kinetic data were obtained from stopped flow measurements with the monochromator set at 310 nm and the slit width set at 1.0 mm. An increase in absorbance due to the formation of the formamidine disulfide ion or its alkyl analogues was observed.

The following stoichiometry was assumed to be correct.

$$2(NH_2)_2CS + H_2O_2 + 2H^+ \rightarrow (NH_2)_2CSSC(NH_2)_2^{\,2+} + 2H_2O$$

This appears to be a valid assumption since it has been verified independently by different sources.[1,2,5,8,9,10] The results presented here also are in agreement with this stoichiometry. The reaction was found to be first order each in thiourea and hydrogen peroxide concentrations. Double-logarithmic plots were used to determine the order of each reactant. Determinations of order conditions were determined by holding the perchloric acid and hydrogen peroxide concentrations in sufficient excess over that of thiourea. The particular species being examined was varied while the concentrations of the two remaining species were held constant.

As predicted by Werner's observation[5] of the instability of the formamidine disulfide ion at low acid concentrations, problems were encountered while following the increase in absorbance due to the formation of the dimeric product. At pH values greater than 1, the formamidine disulfide ion apparently breaks down with the formation of colloidal sulfur. When colloidal sulfur forms in the observation chamber of the stopped flow, there is a drastic increase in light scattering of the reaction solution. The absorbance increases abnormally and erratically before gradually tapering off. As a result, it was necessary to maintain at all times a sufficiently high acid concentration to ensure the stability of the product. Working at high acid concentrations of 2 M or greater has its own consequences. Even for reactions between two neutral molecules or between a neutral molecule and an ion, the rate constant may depend on ionic strength at high ionic concentration.[12]

It has been pointed out[13] that rate laws for the oxidation of many electron pair donors by hydrogen peroxide are of the form

$$\text{rate} = k_2[H_2O_2][N] + k_3[H_2O_2][N][H^+] \tag{3}$$

with k_3 being significantly larger than k_2 in aqueous solution. The existence of these two independent rate terms has been demonstrated for the reaction of hydrogen peroxide with iodide,[14] bromide,[14] chloride,[14,15] iodate,[16] thiosulfate,[17,18] hypoiodite,[19] thiocyanate[20] ions, two *N*-thiocyanatocobalt(III) complexes,[21,22] and two neutral molecules, thiodiglycol[23] and thioxane.[24] The two organic molecules react with *tert*-butyl hydroperoxide by the same rate law[24,25] and presumably by the same mechanism. The reaction of hypochlorite ion[26] with hydrogen peroxide has a rate law which can be interpreted in similar fashion; however, there are several mechanistic possibilities, which include a possible free-radical scheme.[27]

The applicability of this rate law (eq 3) to the reaction of hydrogen peroxide and thioureas was examined. Taking into account the first-order behavior for thiourea and for peroxide, we can write the equation

$$k_\phi = k_2 + k_3[H^+] \tag{4}$$

Table II. Kinetic Data for tu Oxidation as a Function of Acid Concentration and Temperature[a]

Temp, °C	$[H^+]_0$, M	k_{obsd}, s^{-1} [b]	k_ϕ, M^{-1} s^{-1} [b]
25	0.29	0.284	0.563
25	0.58	0.443	0.874
25	1.04	0.783	1.55
25	1.50	1.10	2.18
25	2.00	1.42	2.78
25	2.49	1.78	3.52
25	2.89	2.41	4.35
40	0.29	0.638	1.26
40	0.58	0.986	1.95
40	1.04	1.78	3.53
40	1.50	2.61	5.17
40	2.00	3.44	6.82
40	2.49	4.14	8.19
40	2.89	4.63	9.16

[a] $[tu]_0$ = 0.10 M and $[H_2O_2]_0$ = 0.505 M. [b] Average value for no less than three repeat experiments, with error range never greater than 2%.

Table III. Kinetic Data for detu Oxidation as a Function of Acid Concentration and Temperature[a]

Temp, °C	$[H^+]_0$, M	k_{obsd}, s^{-1} [b]	k_ϕ, M^{-1} s^{-1} [b]
25	0.10	0.0284	0.142
25	0.25	0.0465	0.233
25	0.50	0.0715	0.358
25	1.00	0.113	0.563
25	1.50	0.191	0.955
25	2.00	0.230	1.15
40	0.10	0.0826	0.413
40	0.25	0.119	0.559
40	0.50	0.161	0.804
40	1.00	0.257	1.29
40	1.50	0.400	2.00
40	2.00	0.449	2.50

[a] $[detu]_0$ = 0.02 M and $[H_2O_2]_0$ = 0.2 M. [b] See footnote *b* of Table II.

Table IV. Kinetic Data for dmtu Oxidation as a Function of Acid Concentration and Temperature[a]

Temp, °C	$[H^+]_0$, M	k_{obsd}, s^{-1} [b]	k_ϕ, M^{-1} s^{-1} [b]
25	0.12	0.0420	0.210
25	0.29	0.0535	0.267
25	0.52	0.0773	0.387
25	0.98	0.142	0.711
25	1.50	0.188	0.938
25	2.03	0.259	1.29
40	0.12	0.0935	0.467
40	0.29	0.127	0.634
40	0.52	0.188	0.940
40	0.98	0.314	1.57
40	1.50	0.437	2.18
40	2.03	0.578	2.89

[a] $[dmtu]_0$ = 0.02 M and $[H_2O_2]$ = 0.2 M. [b] See footnote *b* of Table II.

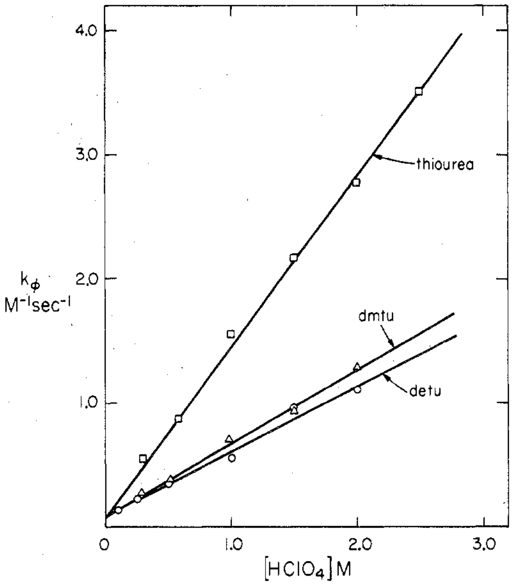


Figure 1. Three plots of pseudo-second-order rate constant against perchloric acid concentration at 25 °C.

Table V. Summary of Rate Data for Thiourea Oxidations[a]

Thiourea	k_3(25 °C)[b]	k_3(40 °C)[b]	$\Delta H^{\ddagger}_3$	$\Delta S^{\ddagger}_3$
tu	1.42	3.21	40	−109
dmtu	0.595	1.28	37	−126
detu	0.534	1.12	36	−130
Thiourea	**k_2(25 °C)[c]**	**k_2(40 °C)**	**$\Delta H^{\ddagger}_2$**	**$\Delta S^{\ddagger}_2$**
tu	0.070	0.26	63	−59
dmtu	0.094	0.29	54	−73
detu	0.086	0.26	54	−80

[a] Units of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are kJ mol^{-1} and J mol^{-1} K^{-1}, respectively. [b] Units of k_3 are M^{-2} s^{-1}. [c] Units of k_2 are M^{-1} s^{-1}.

where k_ϕ is the pseudo-second-order constant. Data contained in Tables II through IV and illustrated in Figure 1 are some results of kinetic runs for tu (thiourea), dmtu (*N,N'*-dimethylthiourea), and detu (*N,N'*-diethylthiourea) which verify the hydrogen ion dependence.

Because of the instability of the dimeric product in weakly acid solution and the fact that the ionic strengths were at a level where specific effects could be important, the intercepts, which correspond to k_2 in Figure 1, may be intrinsically less reliable than those with other nucleophiles. The averaged values for k_2 and k_3 at two different temperatures are listed in Table V. Contrary to what one would predict on the basis of inductive effects alone, the rates of dmtu and detu change more slowly than those of tu as a function of acid concentration. This is reflected most clearly in the k_3 values. However, the k_2 values roughly follow the trend predicted on the basis of inductive effects. Actually, this is not too surprising when the skewed configuration of hydrogen peroxide is considered. In attack of either dmtu or detu on the peroxide oxygen, there is undoubtedly more unfavorable electronic repulsions due to the rotating methyl and ethyl groups. The entropic effect should be most pronounced in the transition state represented by the second term in the rate law. This unfavorable steric arrangement can be visualized with the help of simple space-volume models of hydrogen peroxide and the various substituted thioureas.

The kinetic data in Table V were used to determine activation energies from the Arrhenius equation and these results are also included in Table V. Using the standard equations

$$\Delta H^{\ddagger} = E_a - RT$$

$$\Delta S^{\ddagger} = R\{\ln A - \ln (kT/h) - 1\}$$

where *A* is the frequency factor in the Arrhenius equation, the values of enthalpy and entropy of activation were calculated for each term.

Discussion

Some investigators assume that thiourea exists, predominately as a monoprotonated speices, $NH_2CSNH_3^+$, in highly acidic solutions.[28,29] In the study[30] on which they based their assumptions, the pK_a of thiourea was determined to be 2.03

Table VI. pK_a Values for the Conjugate Acids of Various Thioureas

Compd	pK_a	Compd	pK_a
Thiourea	−1.19[a]	Trimethylthiourea	−1.53[a]
Methylthiourea	−1.12[a]	Ethylenethiourea	−1.90[a]
N,N'-Dimethylthiourea	−1.32[a]	Thiourea	−1.26[b]
N,N-Dimethylthiourea	−1.08[a]	Thiourea	−1.00[c]

[a] M. J. Janssen, *Recl. Trav. Chim. Pays-Bas*, 81, 650 (1962). [b] R. Zahradnik, *Collect. Czech. Chem. Commun.*, 24, 3678 (1959). [c] J. Walker, *Z. Phys. Chem.*, 4, 319 (1889); F. G. Bordwell, "Organic Chemistry", MacMillan, New York, N.Y., 1963, p 868.

in a water–dioxane mixture where the water composition was never greater than 50% of the mixture. The pK_a's of the thioureas have been determined in aqueous solution by different investigators to be in the range of −1 to −1.9 (Table VI). These values were determined from spectrophotometric measurements in sulfuric acid–thiourea solutions of various strengths using a modified form of the Hammett acidity constant treatment for strongly acidic systems. In light of these studies it is reasonable to assume that thiourea is not protonated in the concentration range 0.1 M ≤ [$HClO_4$] ≤ 3.0 M used in the present study.

The electrophilic behavior of hydrogen peroxide toward electron pair donors has been well established. In the reaction of thiourea and hydrogen peroxide, thiourea acts as the nucleophile in a displacement on peroxide oxygen. It has been determined that the oxidation of thiourea follows a two-term rate law and that $k_3 > k_2$. Since each term of the rate law represents a separate transition state, the compositions of the two transition states are $HO_2HSCN_2H_4$ and $HO_2H_2SCN_2H_4^+$.

The role of the proton in the k_3 transition state must be related to the protonation of a peroxide oxygen considering that $k_3 > k_2$ and that H_2O should be a better leaving group than OH^-. Moreover, the equilibrium between hydronium ion and hydrogen peroxide has been reasonably well established and accepted.[31]

$$H_2O_2 + H_3O^+ \rightleftarrows H_3O_2^+ + H_2O$$

In terms of a possible mechanism, the overall order of three in the second term is indicative of the existence of rapid equilibria and of an intermediate before the rate-determining step, and since the stoichiometric coefficient of thiourea exceeds its kinetic order, there is an intermediate after the rate-determining step. A mechanism consistent with the observed rate law for the second-order term is shown in eq I–III with the first step being rate determining. For the third-order term, the proposed mechanism is shown in eq I′–IV′, with step II′ being rate determining. Steps occurring after the rate-determining steps have only been postulated to satisfy the stoichiometric requirements because no direct experimental knowledge can be gained of how the mechanism proceeds after the rate-determining step.

$$H_2O_2 + tu \xrightarrow{k_2} HO(tu)^+ + OH^- \qquad (I)$$

$$HO(tu)^+ + H^+ \rightleftarrows H_2O(tu)^{2+} \qquad (II)$$

$$H_2O(tu)^{2+} + tu \xrightarrow{\text{rapid}} (NH_2)_2CSSC(NH_2)_2^{2+} + H_2O \qquad (III)$$

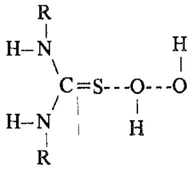
$$H_2O_2 + H^+ \rightleftarrows H_3O_2^+ \qquad (I')$$

$$H_3O_2^+ + tu \xrightarrow{k_3} HO(tu)^+ + H_2O \qquad (II')$$

$$HO(tu)^+ + H^+ \rightleftarrows H_2O(tu)^{2+} \qquad (III')$$

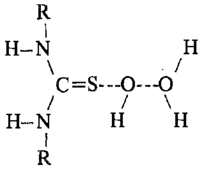
$$H_2O(tu)^{2+} + tu \rightarrow (NH_2)_2CSSC(NH_2)_2^{2+} + H_2O \qquad (IV')$$

In the first mechanism, the rate-determining step involves a heterolytic breakdown of peroxide with hydroxide as the leaving group. A simple model for the transition state (ignoring solvent participation) would be



R = H, CH_3, C_2H_5

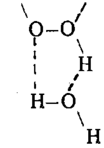
where the thiourea approaches the peroxide along a line formed by the two peroxidic oxygens and the unshared electron pairs in the valence shell of the oxygens are similar in steric behavior to bonded hydrogen atoms. The transition state for the acid-catalyzed term is presumed to have a structure with O–O bond breaking to give water as the leaving group.



R = H, CH_3, C_2H_5

The proposed mechanisms are consistent with the following facts: (1) $k_3 > k_2$: as the basicity of the leaving group decreases, the rate of the reaction increases (i.e., H_2O is a better leaving group than OH^-). (2) Negative entropy of activation values: because of the definite orientation of the reactants in the transition state, negative activation entropies are observed with $\Delta S^\ddagger$ for tu > dmtu > detu. (3) Acid catalysis: because of the presence of unshared electron pairs on the oxygen atoms, the rate is enhanced by specific acid catalysis.

Even though the dominant contributing factor to the large negative entropy of activation is the specificity of orientation in the transition state, other contributing factors are the inequality of the incoming and leaving group nature, the charge separation in the transition state, and the hydration energies. The observed trends in $\Delta S^\ddagger$ values for tu, dmtu, and detu can be explained within the above framework. The unfavorable steric involvement of the methyl and ethyl groups has been previously mentioned. In the case of the hydration energies, a certain amount of the solvent shell around the nucleophile must be stripped off in going from the ground state to the transition state. Since the solvation of polar molecules is weaker as the molecule gets larger, the energy loss on desolvation should be less and the entropy gain should also be less for a larger nucleophile. The thioureas are fairly large polarizable molecules and are, most likely, poorly solvated, whereas the leaving groups which are being released in the transition state are strongly solvated. This inequality of incoming and leaving group nature undoubtedly contributes to the negative entropy of activation. In addition, participation of water in the structure of the transition state[31] must be considered in which the effect of charge separation should be reduced by means of proton transfers in a cyclic activated complex.



From these arguments, the observed trend in k_3 values of tu > dmtu > detu is reasonable. Apparently the entropic factors are sufficient to offset the enthalpic variations.

Table VII lists for comparison the results of a number of peroxide oxidations with various peroxides and donors; a

Table VII. Some Kinetic Data for Acid-Catalyzed Oxidations by Peroxides[a]

R	N[g]	k_2[h]	$\Delta H^{\ddagger}_2$[j]	$\Delta S^{\ddagger}_2$[i]	k_3[k]	$\Delta H^{\ddagger}_3$	$\Delta S^{\ddagger}_3$	k_3/k_2	Ref
H	$S_2O_3^{2-}$	0.025			1.7			68	17, 18
H	I^-	0.011	54	−67	0.32	41	−88	29	14
H	SCN^-	5.2×10^{-4}	62	−105	0.025	44	−134	48	20
H	Br^-	3.8×10^{-7}	86	−46	2.3×10^{-4}	67	−54	610	14
H	Cl^-	1.8×10^{-9}	96	−54	8.3×10^{-7}	84	−46	460	14
H	*b*	2.2×10^{-3}			0.023			10	23
H	*c*	2.6×10^{-3}	54	−113	0.035	46	−121	14	24
H	*d*	5.3×10^{-5}	73	−71	9.8×10^{-4}			19	21
H	*e*	4.6×10^{-5}			1.3×10^{-3}			28	22
t-Bu[l]	*b*	1.4×10^{-4}	59	−121	1.5×10^{-3}	45	−147	11	24
t-Bu[l]	*c*	1.4×10^{-4}	56	−130	1.9×10^{-3}			14	25
H	tu	0.07	62	−59	1.42	40	−109	20	*f*
H	dmtu	0.094	56	−75	0.595	37	−126	6	*f*
H	detu	0.086	56	−80	0.534	36	−130	6	*f*

[a] All data are for ROOH oxidation of N at 25 °C in water. [b] N is bis(β-hydroxyethyl) sulfide. [c] N is thioxane. [d] N is thiocyanatopentaamminecobalt(III) cation. [e] N is thiocyanatonitrobis(ethylenediamine)cobalt(III) cation. [f] This study. [g] N = nucleophile. [h] k_2 in $M^{-1}\ s^{-1}$. [i] $\Delta S^{\ddagger}$ in J mol⁻¹ K⁻¹. [j] $\Delta H^{\ddagger}$ in kJ mol⁻¹. [k] k_3 in $M^{-2}\ s^{-1}$. [l] *t*-Bu = $(CH_3)_3C$.

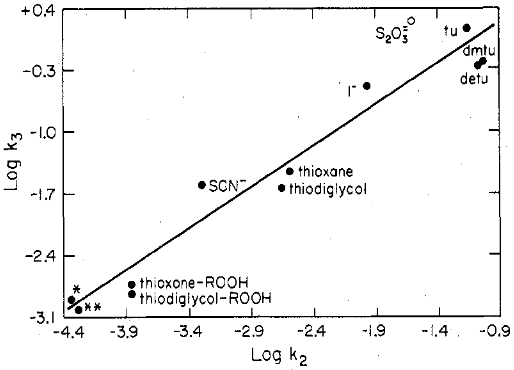


Figure 2. Linear free-energy plot of log k_3 against log k_2 for acid-catalyzed oxidations by peroxides: (*) $Co(en)_2NO_2(NCS)^+$ and (**) $Co(NH_3)_5NCS^{2+}$.

common mechanistic behavior is indicated. The small k_3/k_2 ratios for the thioureas agree reasonable well with the values for the other neutral nucleophiles. Considering only electrostatics, the value of k_3/k_2 should be largest for anionic nucleophiles, intermediate for neutral nucleophiles, and smallest for cationic nucleophiles. Clearly, this is true for anionic nucleophiles, but the difference between neutral and cationic nucleophiles is negligible. There is no clear trend in activation parameters, even though they should be affected by charges.

To the data in Table VII, one new set of related data can be appended. Hiatt and McColeman[32] have found that the oxidation of triphenylphosphine by *n*-butyl hydroperoxide in ethanol at 25 °C follows the same rate pattern. The values obtained are $k_2 = 1.28\ M^{-1}\ s^{-1}$, $k_3 = 24.0\ M^{-2}\ s^{-1}$, and $k_3/k_2 = 19$.

In Figure 2 a linear free-energy plot of log k_3 against log k_2 using the data in Table VII has a slope of 0.95. If the two transition states for the two terms in the empirically determined rate law are related to each other, then a slope, which is close to one, is a clear indication that the mechanisms for the two paths are very similar (i.e., it is probable that the O–O bond in the peroxide reactant is being broken in both transition states). This seems to be a general mechanism for hydrogen peroxide and alkyl hydroperoxide oxidations of electron pair donors, but peroxo acids such as peroxoacetic acid cannot be included in the same category since peroxycarboxylic acids react with a transition state having intramolecular hydrogen bonding.[31]

From the data in Table VII, thiourea shows a higher nucleophilicity toward peroxide oxygen than do iodide and thiosulfate ions; this is apparent from the k_2 values. (The k_3 values have an electrostatic contribution which complicates the interpretation.) This is consistent with the observation that thiourea is a much stronger nucleophile toward square-planar platinum(II) complexes than is iodide ion.[33] The similarity in patterns of nucleophilic reactivity toward peroxide oxygen and platinum(II) complexes has been previously pointed out.[34] A similar comparison of peroxide oxygen, platinum(II) complex, and trivalent nitrogen had been suggested,[35] and our results are in agreement with this correlation.

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Registry No. tu, 62-56-6; dmtu, 534-13-4; detu, 105-55-5; H_2O_2, 7722-84-1; bis(*N*,*N*′-diethyl)dithioformamidine bis(hydrogen bromide), 64035-49-0; $(NH_2)_2CSSC(NH_2)_2^{2+}$, 64035-50-3; $(CH_3NH)_2CSSC(NHCH_3)_2^{2+}$, 64035-51-4; $(C_2H_5NH)_2CSSC(NHC_2H_5)_2^{2+}$, 64035-52-5.

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Reactivity of Coordinated Nitrosyls. 6. Preparation, Characterization, and Reduction of Nitrosylpentaaquoruthenium(3+) and Reduction of Various Ruthenium Ammine Nitrosyls

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A new nitrosyl complex, nitrosylpentaaquoruthenium(II), has been prepared in acidic solution by the direct nitrosylation of $Ru(H_2O)_6^{3+}$ and characterized. The $Cr(H_2O)_6^{2+}$ reductions of $Ru(H_2O)_5NO^{3+}$, $Ru(NH_3)_5NO^{3+}$ in the absence of Cl^-, and several *cis*- and *trans*-tetraammine nitrosyls were found to proceed with a 4:1 stoichiometry to yield stable complexes which have been tentatively formulated as imido-bridged heterometallic dimers: $[(H_2O)L_4Ru{-}\underset{..}{N}H{-}Cr(H_2O)_5]^{5+}$, L = NH_3, H_2O. The formulation of the latter structure is based upon UV–vis and IR spectra, ion-exchange chromatography, and microanalyses. The product analysis indicates that the nitrosyl nitrogen is retained in the bridge, and the presence of Cr(III) in the product suggests that inner-sphere attack by chromium(II) occurs via the nitrosyl entity at some point during the reduction. The chemistry of this new nitrosyl complex, $Ru(H_2O)_5NO^{3+}$, has been compared with that of previous complexes which we have studied; and we have discovered a striking difference in the nature of the products by simply replacing ruthenium for chromium as the metal center. In the reduction of $Ru(NH_3)_5NO^{3+}$ by $Cr(H_2O)_6^{2+}$, the presence of excess Cl^- changes the stoichiometry, rate, and products of the reduction. By replacing ammine with aquo ligands a large rate increase is observed and formation of dimer is unaffected by Cl^-. These observations have been discussed in terms of a possible nitrene intermediate.

Introduction

Transition-metal nitrosyl complexes have been extensively investigated because of the often unique chemical–physical properties of the nitrosyl ligand. Studies of the oxidation–reduction behavior of these nitrosyl complexes provide insight into the reactivity of a ligand capable of undergoing successive stages of reduction through several potentially stable intermediate oxidation states (i.e., $\dot{N}O$, NO^-, N_2, NH_3OH^+, N_2H_4, NH_3).

A decade ago Fraser[3] and Griffith[4] began to delve into the redox behavior of coordinated nitrogen oxides. Griffith[5] first described the reduction of ruthenium nitrosyls with Sn(II) in Cl^- medium. Subsequent investigations of these reductions[6,7] led to the isolation and characterization of novel binuclear nitrido-bridged complexes of ruthenium(IV). A similar study by Mukaido[8] resulted in complexes containing coordinated $SnCl_3^-$ and provided sketchy evidence for a nitrosyl-bridged binuclear ruthenium complex as well as a nitrido-bridged ruthenium(IV) dimer.

More recently, upon reduction of several metal nitrosyls with the common reductant chromium(II) in acidic aqueous solution, we have found that the nitrosyl does indeed react in a variety of ways. Although the mechanisms of reduction appear dissimilar, reduction of $Cr(H_2O)_5NO^{2+}$ [9] and $Cr(NH_3)_5NO^{2+}$ [10] by $Cr(H_2O)_6^{2+}$ resulted in the consumption of 2 equiv of reductant and the formation of 1 equiv of free hydroxylamine. On the other hand, the reduction of $Ru(NH_3)_5NO^{3+}$ [11] in Cl^- medium results in the immediate formation of $Ru(NH_3)_6^{2+}$ via a six-electron reduction.

In this paper, we describe the preparation of a new compound, $Ru(H_2O)_5NO^{3+}$, and detail another mode of reduction in which the $Ru(H_2O)_5NO^{3+}$ consumes 4 equiv of chromium(II) to form a novel chromium–ruthenium dimer. An identical stoichiometry with the formation of a heteronuclear dimer containing a similar chromaphore is also reported herein for the chromium(II) reduction of $Ru(NH_3)_5NO^{3+}$ (in the absence of Cl^-) and *cis*- and *trans*-nitrosyltetraammineruthenium(II) complexes.

Experimental Section

Analyses. Chromium was analyzed spectrophotometrically at 372 nm (ϵ 4815 M^{-1} cm^{-1})[12] after oxidation in alkaline peroxide. In the presence of ruthenium, chromium was analyzed in acidic solution by employing 1,5-diphenylcarbazide (540 nm, ϵ 4 × 10^4 M^{-1} cm^{-1}).[13,14] Our previously mentioned procedure[15] based on the ruthenate–perruthenate method of Woodhead and Fletcher[16] was used for all ruthenium assays. When both chromium and ruthenium were present, a correction for chromium(VI) was made on the basis of the 1,5-diphenylcarbazide analysis for chromium (417 nm, ϵ 680 M^{-1} cm^{-1}).[17] Hydroxylamine was analyzed spectrophotometrically (λ_{max} 368, ϵ 1.4 × 10^4 M^{-1} cm^{-1})[18] after forming the *p*-nitrobenzaldoxime. Ammonium ion was separated from the product mixtures by ion-exchange methods[19] and spectrometrically analyzed as the indophenol (λ_{max} 628, ϵ ~6.6 × 10^4 M^{-1} cm^{-1}) as described previously.[10] Nitrite content was determined by the standard method.[20] Nitrous oxide production was determined by the previously described gas chromatographic procedure.[21] The solubility of N_2O in aqueous solution was accounted for by preparing standard solutions of N_2O.

Preparations. Solutions of $Cr(H_2O)_6^{3+}$ in $TFMS^-$ medium were prepared by the peroxide reduction of CrO_3 in the presence of HTFMS.[22] The corresponding $Cr(H_2O)_6^{2+}$ solutions were prepared and standardized as previously reported.[9] Trifluoromethylsulfonic acid (HTFMS) (3M Corp.) was distilled under vacuum at 10 Torr at 62 °C and diluted immediately to a concentration of 3 M and stored in a polyethylene bottle. NaTFMS was prepared by the procedure of Scott.[22]

Complexes. **$[Ru(NH_3)_5NO]Cl_3$** was prepared either by reaction of NO(g) with solutions of $[Ru(NH_3)_6]Cl_3$ [23] or by the procedure of Gleu.[24] In order to exclude Cl^- impurity, $[Ru(NH_3)_5NO](TFMS)_3$ was prepared by the following method. Fifty milligrams of $[Ru(NH_3)_5NO]Cl_3$ was completely dissolved in approximately 50 mL of H_2O and placed on a 1/2 in. × 1 in. SP Sephadex C25 cation-exchange column resulting in an orange band. The column was washed with water until several drops of $AgNO_3$ added to the rinse no longer indicated the presence of Cl^-. The $Ru(NH_3)_5NO^{3+}$ was then quickly removed from the column with 25 mL of 1.0 M NaTFMS (0.1 M