

Another point of interest is the deviation of the $[\text{Ru}(\text{en})_3]^{2+}$ reaction from the LFER. While there has been no satisfactory direct measurement of k_{22} for the $[\text{Ru}(\text{en})_3]$ couple, the value has been estimated as being about fivefold greater than for the $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ couple.³⁹ This difference accounts for about half of the observed deviation in the LFER, and so the reaction is not considered to be anomalous.

In summary, the reduction of O_2 by a series of ruthenium amines proceeds by one-electron outer-sphere electron transfer. The rates conform to the Marcus theory, and they lead to an estimate of the self-exchange rate for the O_2/O_2^- couple.

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Registry No. $[\text{Ru}(\text{NH}_3)_4\text{phen}](\text{TFMS})_2$, 69799-60-6; *trans*- $[\text{Ru}(\text{NH}_3)_4\text{isn}(\text{H}_2\text{O})](\text{PF}_6)_2$, 72214-11-0; $[\text{Ru}(\text{NH}_3)_5\text{isn}](\text{ClO}_4)_2$, 31279-70-6; $[\text{Ru}(\text{NH}_3)_5\text{isn}](\text{TFMS})_3$, 72214-12-1; *trans*- $[\text{Ru}(\text{NH}_3)_4\text{isnCl}]^+$, 63323-68-2; *cis*- $[\text{Ru}(\text{NH}_3)_4\text{isn}(\text{H}_2\text{O})]^{2+}$, 60168-57-2; $[\text{Ru}(\text{NH}_3)_6]^{2+}$, 19052-44-9; $[\text{Ru}(\text{en})_3]^{2+}$, 21393-86-2; O_2 , 7782-44-7; $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}](\text{TFMS})_3$, 53195-18-9; *trans*- $[\text{Ru}(\text{NH}_3)_4\text{isn}(\text{SO}_4)]\text{Cl}$, 60209-67-8; $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, 18532-87-1; $[\text{Ru}(\text{NH}_3)_5\text{isn}]^{2+}$, 19471-53-5; $[\text{Ru}(\text{NH}_3)_4\text{phen}]^{2+}$, 69799-59-3; *trans*- $[\text{Ru}(\text{NH}_3)_4\text{isn}(\text{H}_2\text{O})]^{2+}$, 60208-50-6; $[\text{Ru}(\text{NH}_3)_5(4\text{-vinyl-py})]^{2+}$, 60166-34-9.

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A Kinetic Study of the Oxidation of a Series of *N*-Alkylphenothiazines by Neptunium(VI) in Aqueous Perchlorate Media¹

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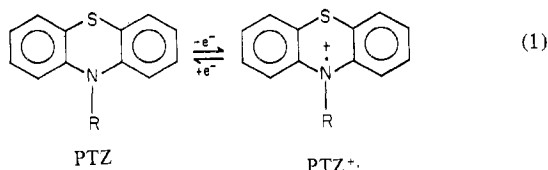
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The kinetics of oxidation of a series of *N*-alkylphenothiazines to the corresponding cation radicals by means of neptunium(VI) have been studied by a stopped-flow spectrophotometric technique. The reaction rates are first order in both of the reagents and are independent of acidity. A linear relation between ΔG^\ddagger and ΔG^* for the title series of reactions is observed. Values of the rate parameters calculated from the Marcus theory are about 100 times greater than the experimental values. There is also a marked discrepancy between experimental and calculated values of ΔH^* and ΔS^* .

Introduction

In a previous kinetic study of the oxidation of *p*-hydroquinone and *p*-toluhydroquinone by $\text{Np}(\text{VI})$ in aqueous perchlorate media⁴ an apparent agreement between the experimental values of the rate parameters and those calculated by using the Marcus⁵ cross relations was noted. In that study the product of the 1-equiv oxidation of $\text{Np}(\text{VI})$ was an unstable intermediate radical species, and there is a consequent ambiguity in the value estimated for the self-exchange parameter required for the Marcus type calculation.

In contrast, the *N*-alkylphenothiazines (PTZ) are oxidized to stable cation radicals through a 1-equiv step⁶



By varying the alkyl chain R or the substituents on the aromatic nuclei it is possible to vary the free-energy change of (1). The detailed dynamic studies of the oxidation of a number of such compounds by the aquometal ions $\text{Fe}(\text{III})$,⁷ $\text{Co}(\text{III})$,⁸ and $\text{Fe}(\text{CN})_6^{3-7}$ have provided thermodynamic and dynamic

data that are useful in analyzing the present results with $\text{Np}(\text{VI})$ as the oxidant in terms of the Marcus theory.

Experimental Section

Reagents. The *N*-alkylphenothiazines (Table I) used in this investigation were available from the laboratory reserves of E.P. The purity of these compounds had been verified by elemental analysis as well as by mass spectrometry and NMR spectra. The preparation and standardization of the perchloric acid, lithium perchlorate, and neptunium(VI) perchlorate solutions have been previously described.⁹ All solutions were prepared in triply distilled water.

Equipment and Procedures. The computer-interfaced stopped-flow instrumentation, as well as the basic procedures and techniques, has been detailed previously.¹⁰ The observed OD vs. t data from individual kinetic experiments were treated by standard nonlinear least-squares techniques in terms of the first-order rate expression

$$\text{OD}_t = (\text{OD}_0 - \text{OD}_\infty) \exp(-k_{\text{obsd}}t) + \text{OD}_\infty$$

where k_{obsd} , OD_0 , and OD_∞ are adjustable parameters. Each kinetic experiment was monitored to at least 90% completion, 800-950 data points being collected during this period. A minimum of seven experimental determinations of k_{obsd} were made for each set of reaction conditions.

The range of initial concentration was chosen to ensure first-order conditions, $[\text{PTZ}]_0 = 5.0 \times 10^{-6} - 1.0 \times 10^{-5}$ M and $[\text{Np}(\text{VI})]_0 = 5.0 \times 10^{-5} - 2.0 \times 10^{-4}$ M. The kinetic experiments were monitored at the wavelength of maximum absorption of the cation radicals, listed in Table I. None of the other species involved in the reaction have an appreciable absorptivity at the chosen wavelengths.

Results

Stoichiometry. For the reactions



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(1) Work performed under the auspices of the Office of Basic Energy Sciences of the Department of Energy.

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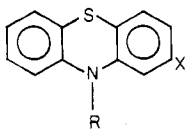
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Table I. Reduction Potentials of Investigated Phenothiazines and Spectral Characteristic of the Corresponding Cation Radicals⁷

compd	X	R	$E^{\circ}, ^a \text{V}$	λ, nm	$10^{-3}\epsilon, \text{M}^{-1} \text{cm}^{-1}$
I	OH	$\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	0.62 ₅	562	9.5
II	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	0.71 ₅	513	9.2
III	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{-c-N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$	0.72	514	9.4
IV	Cl	$\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	0.78	525	10.2
V	H	$\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	0.82	511	10.5
VI	H	$\text{CH}_2\text{CH}(\text{CH}_3)\text{N}(\text{CH}_3)_2$	0.86 ₅	515	9.3
VII	H	$\text{CH}(\text{CH}_3)\text{CH}_2\text{N}(\text{CH}_3)_2$	0.89	524	8.8

^a Determined from equilibrium quotients with Fe(III) at 25.0 °C, $[\text{HClO}_4] = 1.00 \text{ M}$, and $\mu = 1.0 \text{ M}$.

Table II. Rate Constants at Different Temperatures and Activation Parameters for Reaction of Phenothiazines with Neptunium(VI)

compd	$10^{-4}k^a$			$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$
	2.0 °C	25.0 °C	35.1 °C		
I		360 ± 10^d			
II	73.3 ± 1.8	160 ± 2	230 ± 5	5.2 ± 0.3	-12.8 ± 1.0
III	60.1 ± 0.8	133 ± 3	186 ± 7	5.1 ± 0.1	-13.0 ± 1.0
IV	35.4 ± 0.9	88.5 ± 2.3	102 ± 7	5.6 ± 0.6	-12.7 ± 2.2
V	9.31 ± 0.17	23.6 ± 0.3	32.6 ± 0.3	5.8 ± 0.2	-14.6 ± 0.7
VI	6.75 ± 0.08	19.1 ± 0.6	26.3 ± 0.4	6.4 ± 0.2	-13.1 ± 0.6
VII	8.65 ± 0.20	21.5 ± 0.2	29.3 ± 0.7	5.7 ± 0.3	-14.9 ± 0.9

^a $\text{M}^{-1} \text{s}^{-1}$; error listed as standard deviation of the mean; $[\text{HClO}_4] = 1.0 \text{ M}$, $\mu = 1.0 \text{ M}$. ^b kcal mol^{-1} . ^c $\text{cal deg}^{-1} \text{mol}^{-1}$. ^d Second-order conditions. Rate parameter determined graphically.

the values for the potentials of the reductants (listed in Table I) and the known value of 1.137 V for $\text{Np(VI)}/\text{Np(V)}$ provide the necessary evidence that the reactions will go to completion. This stoichiometry was verified for initial conditions of excess PTZ by spectrophotometric determination of the product radical ions. Within the limits of our experimental uncertainties ($\pm 5\%$) the ratio $\Delta[\text{PTZ}^{\cdot+}]/\Delta[\text{Np(VI)}] = 1$.

Kinetics. The integrated form of the first-order rate law provided an adequate description of the experimental data. In addition, second-order rate parameters determined with excess of either reagent were in substantial agreement. For example, at 25 °C, 1.00 M HClO_4 , and initial concentrations of compound VI (Table I) and Np(VI) , M, of 1.00×10^{-5} and 1.58×10^{-4} ; 2.00×10^{-4} and 1.26×10^{-5} ; and 3.00×10^{-4} and 1.26×10^{-5} the respective values calculated for the second-order rate parameters, $\text{M}^{-1} \text{s}^{-1}$, are $(1.96 \pm 0.02) \times 10^5$, $(1.89 \pm 0.03) \times 10^5$, and $(1.89 \pm 0.04) \times 10^5$. All these observations are consistent with the formulation of the empirical rate law as

$$d[\text{PTZ}^{\cdot+}]/dt = k[\text{PTZ}][\text{Np(VI)}] \quad (3)$$

The data presented in the tables are average values of the second-order rate parameters determined over similar concentration ranges for each compound. The uncertainties are standard deviations.

When Np(VI) is the reagent originally in excess, an additional reaction can be observed leading to the disappearance of the cation radicals, probably due to further oxidation of the original product to the corresponding dication.⁴ This reaction is, however, 2–3 orders of magnitude slower than those reported in this study and does not interfere with the evaluation of the rate parameters of (3).

The variation of the rate parameter, at an ionic strength of 1.0, as a function of perchloric acid concentration was determined for compounds IV and VI. The results are presented in Table III.

In Table IV, the change in rate parameter with variation in ionic strength at an acidity of 0.010 M perchloric acid is listed for compound VI.

Table III. Effect of Acidity on the Reaction Rate of Phenothiazines with Neptunium(VI)^a

compd	$10^{-5}k, \text{M}^{-1} \text{s}^{-1}$		
	$[\text{H}^+] = 1.00 \text{ M}$	$[\text{H}^+] = 0.10 \text{ M}$	$[\text{H}^+] = 0.010 \text{ M}$
IV	8.85 ± 0.23	10.4 ± 0.15	10.0 ± 0.1
VI	1.91 ± 0.06	2.22 ± 0.04	2.14 ± 0.02

^a 25.0 °C, $\mu = 1.0 \text{ M}$ (LiClO_4).

Table IV. Ionic Strength Effect on the Reaction Rate of Compound VI with Neptunium(VI)

$\mu, ^a \text{M}$	$10^{-4}k, \text{M}^{-1} \text{s}^{-1}$	$\mu, ^a \text{M}$	$10^{-4}k, \text{M}^{-1} \text{s}^{-1}$
0.010	4.41 ± 0.08	0.050	6.44 ± 0.04
0.020	5.00 ± 0.07	0.100	8.38 ± 0.09
0.030	5.53 ± 0.04		

^a $[\text{HClO}_4] = 0.010 \text{ M}$; ionic strength adjusted with LiClO_4 , 25 °C.

Table V. Experimental and Calculated Rate Constants for Reaction of Phenothiazines with Neptunium(VI)

compd	k_{exptl}^a	$k_{\text{calcd}}^{a,b}$	$k_{\text{calcd}}/k_{\text{exptl}}$
I	3.6×10^6	5.8×10^8	1.6×10^2
II	1.60×10^6	1.8×10^8	1.1×10^2
III	1.33×10^6	1.7×10^8	1.3×10^2
IV	8.85×10^5	7.2×10^7	81
V	2.36×10^5	4.1×10^7	1.7×10^2
VI	1.91×10^5	2.1×10^7	1.1×10^2
VII	2.15×10^5	1.4×10^7	65

^a $\text{M}^{-1} \text{s}^{-1}$; 25.0 °C, $[\text{HClO}_4] = 1.00 \text{ M}$, $\mu = 1.0 \text{ M}$. ^b Calculated according to eq 4, by neglecting the work terms, with $\Delta G^{\ddagger} = 3.3 \text{ kcal mol}^{-1}$ for $\text{PTZ}^{\cdot+}/\text{PTZ}^{\cdot}$ and $\Delta G^{\ddagger} = 12.4 \text{ kcal mol}^{-1}$ for $\text{Np(VI)}/\text{Np(V)}$.¹³

Discussion

The data presented define the empirical formula of the activated complex as one molecule of each of the reactants. The absence of any marked dependence of the rate on the concentration of hydrogen ion demonstrates that there are no hydrogen ion dependent preequilibria over the range of acid

Table VI. Thermodynamic and Activation Parameters for Reactions of Phenothiazines with Neptunium(VI)^a

compd	ΔH°_{12} ^{b,d}	ΔS°_{12} ^{c,d}	ΔH^\ddagger_{12}		ΔS^\ddagger_{12}	
			exptl ^b	calcd ^{b,e}	exptl ^c	calcd ^{c,e}
I	-14.8	-12		-1.0		-22
II	-14.2	-17	5.2 ± 0.3	-1.1	-12.8 ± 1.0	-25
III	-15.7	-21	5.1 ± 0.1	-1.6	-13.4 ± 0.2	-26
IV	-12.4	-11	5.6 ± 0.6	-0.7	-12.7 ± 2.2	-24
V	-12.4	-18	5.8 ± 0.2	-0.8	-14.6 ± 0.7	-27
VI	-12.4	-20	6.4 ± 0.2	-0.9	-13.1 ± 0.6	-28
VII	-11.5	-18	5.7 ± 0.3	-0.6	-14.9 ± 0.9	-27

^a 25.0 °C, [HClO₄] = 1.00 M, μ = 1.0 M. ^b kcal mol⁻¹. ^c cal deg⁻¹ mol⁻¹. ^d Calculated from ΔH° and ΔS° for PTZ/Fe(III) systems, by assuming $\Delta H^\circ = -9.7$ kcal mol⁻¹ and $\Delta S^\circ = +24.5$ cal deg⁻¹ mol⁻¹ for the Fe(III)/Fe(II) system¹⁷ and $\Delta H^\circ = -28.1$ kcal mol⁻¹ and $\Delta S^\circ = -6.4$ cal deg⁻¹ mol⁻¹ for the Np(VI)/Np(V) system.¹⁸ ^e Calculated according to eq 8 and 9, by adopting $\Delta H^\ddagger = 8.05$ kcal mol⁻¹ and $\Delta S^\ddagger = -14$ cal deg⁻¹ mol⁻¹ for Np(VI)/Np(V) self-exchange¹⁶ and $\Delta H^\ddagger = 1$ kcal mol⁻¹ and $\Delta S^\ddagger = -8$ cal deg⁻¹ mol⁻¹ for PTZ⁺/PTZ self-exchange.⁷

studied. The small variations in rate parameters that were observed can be attributed to a "medium" effect.⁸ The same invariance of rate parameter with change in hydrogen ion concentration has also been observed with Fe(III)⁷ and Co(III)⁸ as oxidants.

The data that describe the change in the rate parameter with variation of ionic strength can be correlated in terms of the extended form of the Debye-Hückel equation with the parameters summarized by Newton.¹¹ Since the PTZ's are protonated at the nitrogen atom on the side chain¹² over the acidity range in this work, the value of Δz^2 is 4 for the net activation process, and using the value of $\dot{a} = 0.83$ nm¹¹ and $C = 0.173$ M⁻¹, we calculate an average value of $k_0 = (3.33 \pm 0.29) \times 10^4$ M⁻¹ s⁻¹. These values of the parameters do not provide an optimal fit of the experimental results—a point noted by one of the reviewers. The important aspect of the calculation is that the ionic strength dependence of the reaction rate can be described in terms of the extended Debye-Hückel equation without using any adjustable parameters that are characteristic solely of the present system.

It is evident from the data presented in Tables I and II that the reaction rates decrease from compound I to compound VII, i.e., with an increase of the reduction potentials of the PTZ⁺/PTZ couples. In fact a plot of the values of the free energies of activation ΔG^*_{12} vs. the thermodynamic free energy changes for the respective reactions is linear. Such a linear relationship is expected from the reduced form of the Marcus cross relations. The observed linearity led us to carry out detailed calculations to determine if a quantitative description of these reactions can be provided by theory. The equations used are

$$\Delta G^*_{12} = w_{12} + \lambda_{12}(1 + \Delta G^\circ_{12}/\lambda_{12})^2/4 \quad (4)$$

in which

$$\lambda_{12} = 2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22}) \quad (5)$$

$$\Delta G^\circ_{12} = \Delta G^\circ_{12} + w_{21} - w_{12} \quad (6)$$

$$k = Z \exp(-\Delta G^*_{12}/RT) \quad (7)$$

where Z is the collision frequency in solution, assumed to be 10^{11} M⁻¹ s⁻¹, and the w_{ij} are the appropriate work terms.

The results of such a calculation are summarized in Table V, where the work terms have been neglected due to the difficulties attendant in the evaluation of such terms for a nonspherical reagent in the high ionic strength media used in this investigation. This approximation, neglecting the work

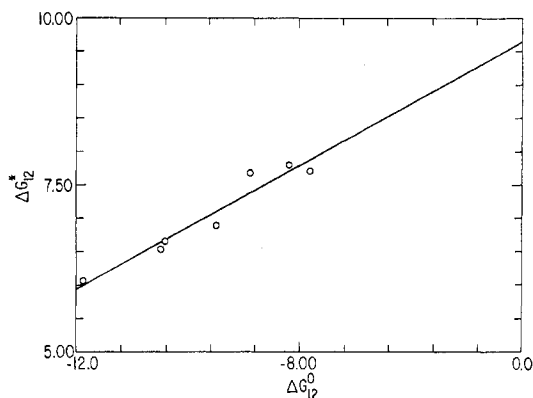


Figure 1. ΔG^*_{12} vs. ΔG°_{12} . Data were obtained from Table V. The least-squares straight line has a slope of 0.31 ± 0.03 and an intercept of 9.6 ± 0.3 .

terms, does not appear to have any systematic effect on the correlation between theory and experiment as noted in an extensive survey of electron-transfer reactors.¹⁴ It is evident from these results that the calculated values of the rate parameters are consistently greater than the experimental values, a result similar to that noted recently¹⁴ for a series of electron-transfer reactions between 2+ and 3+ ions.

Chou, Creutz, and Sutin¹⁴ also suggested that it may be possible to gain insight into the reasons for discrepancies between calculated and observed rate parameters by a comparison of calculated and experimental activation parameters using the relations¹⁵

$$\Delta H^*_{12} = \left(\frac{\Delta H^*_{11}}{2} + \frac{\Delta H^*_{22}}{2} \right) (1 - 4\alpha^2) + \frac{\Delta H^\circ_{12}}{2} (1 + 2\alpha) \quad (8)$$

$$\Delta S^*_{12} = \left(\frac{\Delta S^*_{11}}{2} + \frac{\Delta S^*_{22}}{2} \right) (1 - 4\alpha^2) + \frac{\Delta S^\circ_{12}}{2} (1 + 2\alpha) \quad (9)$$

where $\alpha = \Delta G^\circ_{12}/4(\Delta G^*_{11} + \Delta G^*_{22})$.

Table VI collects the results as well as the detailed information necessary for such calculations. There is obviously a marked discrepancy between experimental and calculated values for both the activation parameters. While some of this

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The relationship between ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger and the usually experimentally derived quantities ΔG° , ΔH° , and ΔS° is of the form: $\Delta G^\ddagger = \Delta G^\circ - RT \ln(\hbar Z/kT)$; $\Delta H^\ddagger = \Delta H^\circ - 1/2 RT$; $\Delta S^\ddagger = \Delta S^\circ + R \ln(\hbar Z/kT) - 1/2 R$.

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lack of correlation may be a reflection of the uncertainties in the data used in the calculations, the idea previously advanced that the actinide electron-transfer reaction may be nonadiabatic¹⁹ could well be a factor in the discrepancy between calculated and observed values of the entropies of activation.

In summary, the linear relationship observed between the ΔG° and ΔG^* for the series of related reactions between Np(VI) and selected phenothiazines is qualitatively accommodated by the Marcus theory of outer-sphere electron-transfer reactions. Quantitative comparisons between values

calculated by the use of this theory and the experimental results do not provide compelling evidence that these systems conform to the criteria necessary for such calculations. Additional studies with isostructural Pu(VI) and/or Am(VI) as oxidants for selected phenothiazines should provide additional insight into the delineation of nonadiabaticity as a source of some of the discrepancies since they will provide a wider range of ΔG° values.

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Registry No. I, 3926-64-5; II, 58-40-2; III, 84-97-9; IV, 50-53-3; V, 60-91-3; VI, 60-87-7; VII, 303-14-0; NpO₂²⁺, 18973-22-3.

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Phase Equilibria in the Samarium-Oxygen-Carbon System. The Existence of Trisamarium Monocarbide

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Composition and vaporization studies in the temperature range 1400–2200 K show that four condensed phases exist in the binary and ternary regions of the Sm–O–C system. A CaC₂-type dicarbide, a nonstoichiometric Pu₂C₃-type phase between SmC_{1.36} and SmC_{1.45}, and a stoichiometric NaCl-type oxide carbide near the SmO_{0.5}C_{0.4} and Sm₂O₃ are observed. The Pu₂C₃-type carbide, SmC₂, vaporizes to form Sm(g) and SmC₂(s), which in turn vaporizes to Sm(g) + C(s). The vaporization products of the oxide carbide are Sm(g) + SmC₂(s) + Sm₂O₃(s). The cubic lattice parameter and the carbon content of SmC₂ decrease with increasing equilibration temperature. Hydrolysis data for SmC₂ indicate that its carbide species are a mixture of diatomic (acetylide) and monoatomic (methanide) ions; its nonstoichiometric behavior is consistent with a mechanism of anion intervalence based on an acetylide-methanide equilibrium process. SmO_{0.5}C_{0.4} is best described as an oxide methanide containing randomly distributed anion vacancies. The present results fail to confirm the existence of a metal-rich carbide near the Sm₃C composition and suggest that the phase observed in an earlier study was actually the oxide carbide.

Introduction

An interest in the high-temperature properties of the lanthanide carbide systems has been promoted by their importance to nuclear reactor technology. The formation of carbides by the reaction of lanthanide fission products with carbide fuels or graphite moderator materials is expected. Additional interest in the carbides has developed because of increased metallurgical applications of the lanthanides in steels and other alloys. The early work of Spedding et al.¹ remains as the most comprehensive investigation of the phase equilibria and structural properties of the carbides, which include the CaC₂-type dicarbides, the Pu₂C₃-type dimetal tricarbides, and Fe₄N-type trimetal monocarbides. Much of the subsequent work has concentrated on the vaporization behavior and thermodynamic properties of the dicarbides.

The samarium system is an attractive candidate for an in-depth study of the equilibrium and thermodynamic properties of the carbides. This system is of particular interest because Sm is an effective neutron poison. The development of suitable fuel reprocessing procedures is based on an adequate understanding of the Sm–C system. The equilibria and structural properties of the samarium carbides have been re-investigated by Lallement et al.² and by Venet and co-workers.^{3,4} Since only small variations are reported for the lattice parameter of SmC₂, Sm₂C₃, and Sm₃C, the existence of well-defined two-phase regions is implied, and the measure-

ment of equilibrium vapor pressures in those regions should be possible.

The initial objective of this study was the determination of the thermodynamic properties of the samarium carbides. However, the results of our preliminary preparative and vaporization experiments were substantially inconsistent with the anticipated behavior. A reinvestigation of the phase equilibria and properties of the Sm–C system was initiated. After subsequent results demonstrated that low levels of oxygen contamination were important, the study was expanded to the oxygen-containing ternary system. In evaluation of our results, an attempt has been made to consider both the equilibrium behavior and the crystal chemistry of the phases in the Sm–O–C system.

Experimental Section

Materials. Samarium chips were freshly cut from ingot metal (99.9% Rare Earth Research Corp.). Powdered graphite was prepared by dry machining of spectrographic grade rods (Ultra Carbon) and vacuum degassing at 2000 °C. Sm₂O₃ (99.99%, American Potash and Chemical Co.) was calcined and stored in sealed containers over Ascarite.

Preparative Procedures. The carbides were prepared by weighing Sm and C in the proper ratios to give compositions in the range 0.3

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