3. No loss of TRIEN dependence was observed at high concentration in these studies, and thus it is concluded that the proton-assisted nucleophilic displacement is not a major contributor. For this pathway to be operative, the lability of the termain group would have to be reduced sufficiently to stabilize outside protonation of the imide linkage. Coordination of the imidazole nitrogen in $CuH_{-2}GGHis^-$ achieves this whereas the carboxylate donor in $CuH_{-2}GGG^-$ is too labile. These studies indicate that the terminal amine coordination in $CuH_{-2}DGEN$ is also too labile and general-acid catalysis is the observed reaction for H_3trien^{3+} and H_2trien^{2+}.

Mechanism for the Reaction of EDTA with $CuH_{-2}DGEN$. $EDTA^{4-}$ in general is not a good nucleophilic ligand for the replacement of polypeptide ligands from the copper(II) and nickel(II) complexes. This is observed in these studies, where k_{EDTA} is too small to be determined. Values were obtained for the two protonated species $HEDTA^{3-}$ and H_2EDTA^{2-} and are consistent with these two ligands acting as acids. These ligands may act as coordinating acids and as a consequence exhibit larger rate constants than expected. This does not appear to be the case for H_2EDTA^{2-} but may be for $HEDTA^{3-}$.

Conclusions

The reaction of $CuH_{-2}DGEN$ with TRIEN and EDTA proceeds through nucleophilic and proton-transfer-limited pathways. The presence of terminal amine groups reduces the reactivity through the nucleophilic and solvent-assisted pathways as compared to that for the similar copper-triclycine complex. This is not the case for the proton-transfer reaction, where the rate constants are comparable to those observed for the other analogous polypeptide complexes.

Registry No. $CuH_{-2}DGEN$, 15156-44-2; trien, 112-24-3; EDTA, 60-00-4.

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Thermodynamic Study and Stabilities of Complex Dicerium Carbide Molecules

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The composition of the vapor phase above the cerium-graphite system was investigated in the temperature range 2100-2800 K by means of Knudsen-effusion mass spectrometry. The molecules Ce, Ce_2C, Ce_2C_2, Ce_2C_3, Ce_2C_4, Ce_2C_5, and Ce_2C_6 were shown to exist in the vapor phase above the liquid solution. Third-law enthalpy changes were evaluated for the following equilibrium reactions: $Ce_2C_n(g) = 2Ce(g) + nC(graph)$. These values were then combined with ancillary literature data to give the atomization energies, $\Delta H_a{}^\circ{}_0$ (kJ mol^{-1}), and the standard enthalpies of formation, $\Delta H_f{}^\circ{}_{298.15}$ (kJ mol^{-1}), of the various polyatomic carbide molecules: Ce_2C, 1047 ± 26, 506 ± 26; Ce_2C_2, 1690 ± 25, 576 ± 25; Ce_2C_3, 2332 ± 28, 647 ± 28; Ce_2C_4, 3076 ± 25, 615 ± 25; Ce_2C_5, 3654 ± 32, 750 ± 32; Ce_2C_6, 4347 ± 36, 770 ± 36.

Introduction

Experimental investigations of the equilibrium vapor above metal-graphite systems by Knudsen cell mass spectrometry over the last two decades have resulted in the thermodynamic characterization of a number of stable gaseous carbides. These have been reviewed in several summaries.[1-4] More recent investigations have shown that the metal carbide vapors are surprisingly quite complex in composition and may contain polyatomic metal carbide species with up to nine atoms.[5-9]

Except for a few preliminary reports,[5,7c,10] very little is known about dimetal carbides of electropositive transition metals. Only the molecules Ce_2C_n (n = 1-6), La_2C_n (n = 1-6), and Ti_2C_4 have been observed and their approximate atomization energies presented. The molecules M_2C_4 are found to have a vapor concentration approximately equal to that of the penta- and hexacarbides. The concentrations of the remaining dimetal carbides are approximately an order of magnitude less than the concentrations of the dimetal tetracarbides.

The above examples amply demonstrate the very complex nature of the vapors above electropositive transition-metal-graphite systems at high temperatures. It is seen in numerous instances that if a stable dicarbide exists, a whole series of metal-carbon species may be observed of the type MC_n and M_2C_n at high temperatures. The knowledge of the vapor composition is functional to the description of the vaporization thermodynamics of any system and is of considerable technological and scientific interest.

As part of our continued research concerned with the identification and the thermodynamic properties of gaseous carbide systems, we have investigated the system cerium-carbon by Knudsen-effusion mass spectrometry. We have previously reported and evaluated thermodynamic values for the gaseous monocerium carbides, within the temperature range 2100-2800 K.[5] The following report is a discussion of the observed gaseous dicerium carbides, which we observed at the higher temperatures in conjunction with previously reported molecules.

Experimental Section

The mass spectrometer employed for this investigation is a single-focusing, 12-in. radius, magnetic deflection, 90° sector, Knudsen cell, high-temperature instrument (Nuclide Model 12-90-HT). The general methods of high-temperature Knudsen-effusion mass spectrometry have been presented in several reviews.[3,11,12] The specific mass spectrometer and experimental arrangements are described more

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Table I. Measured Ion Intensities for the Gaseous Molecules Ce_2C_n (n = 1-6)

		ion intensities, 10^{-11} A						
data[a] set	temp, K	Ce^+	Ce_2C^+	$Ce_2C_2^+$	$Ce_2C_3^+$	$Ce_2C_4^+$	$Ce_2C_5^+$	$Ce_2C_6^+$
1 (27)	2609	3552				0.330		
2 (29)	2631	3859				0.419		
3 (30)	2631	4221				0.450		
4 (42)	2589	2906				0.285		
5 (43)	2589	3045				0.299		
6 (44)	2665	5391		0.033		0.543		
7 (45)	2665	5584		0.050		0.966		
8 (47)	2699	5504		0.068		1.188		
9	2732	6315				1.023		
10 (49)	2732	6440		0.073		1.780		
11 (50)	2732	6714				1.490		
12 (51)	2770	6689				1.830		
13	2733	7913				2.284		
14 (55)	2733	8362	0.045	0.099	0.120	2.148	0.077	0.069
15 (56)	2770	1416	0.078	0.022	0.305	3.530	0.128	0.135
16	2784	1384				3.810		
17 (57)	2784	1381	0.088	0.029	0.288	2.540	0.244	0.150

[a] Data set number in parentheses corresponds to the number in the paper on CeC_n (n = 1-6) molecules, ref 5b.

fully elsewhere.[13,14] Specific instrument operating conditions were 20-V electron energy, 1-mA electron emission current, 4.5-kV accelerating voltage, and 0.26-mA dynode string current.

The pertinent ions were determined by their shutter effect, m/e ratio, isotopic distribution, and ionization efficiency curves (where possible). The observed ion intensities for the gaseous ions Ce^+, Ce_2C^+, $Ce_2C_2^+$, $Ce_2C_3^+$, $Ce_2C_4^+$, $Ce_2C_5^+$, and $Ce_2C_6^+$ are listed in Table I. The lack of a systematic temperature trend in the evaluated third-law values for Ce_2C_4 and Ce_2C_2 together with the reported low appearance potential of 5.9 ± 1.0 and ≤7.0 ± 2.0 eV, respectively, support that the species are primary species and fragmentation contributions, if any, are neglibile within the accuracy of measurements. The data set numbers in parentheses correspond directly to the numbers employed in the earlier paper on the gaseous molecules CeC_n, where n = 1-6.[5b] The reported Ce^+ ion intensities, in Table I, do not always correspond to the Ce^+ ion intensities listed in the previous paper.[5b] The Ce^+ intensities at a given temperature were monitored at various intervals, and the observed intensity of Ce^+ closest to the desired data was employed in the evaluation of the thermodynamic equilibria.

A reference calibration constant, $k_{Ag} = 0.323$ atm A^{-1} K^{-1}, was obtained from the equilibrium dissociation of $Ag_2(g) = 2Ag(g)$, where the enthalpy change of this reaction was taken as $\Delta H^\circ_0 = 159 \pm 6.3$ kJ mol^{-1}, from published data.[15] The pressure constants of the remaining pertinent species were calculated by use of the relation

$$k_i = k_{Ag}(\sigma_{Ag}\gamma_{Ag}n_{Ag}E_i)/(\sigma_i\gamma_iE_{Ag}n_i)$$

where σ, γ, n, and E are the ionization cross section, the multiplier gain, the correction for fractional isotopic distribution, and the intensity correction factor, respectively. The maximum atomic ionization cross sections were taken directly from Mann.[16] Those for the molecular species were estimated as the sum of the atomic cross sections. Multiplier gains were measured for the most intense observable ion current (Ce^+, CeC_2^+) by use of a Faraday cup. For the ions of relatively small intensity, direct measurement of the multiplier gain was not possible; but for these molecules the multiplier gain was assumed equal to that of CeC_2^+. The factor E was evaluated from $I^+_{max}/I^+_{(20\ eV)}$ from the measured ionization efficiency curves. The resulting pressure constants are $Ce^+ = 0.053$, $Ce_2C^+ = 0.027$, $Ce_2C_2^+ = 0.025$, $Ce_2C_3^+ = 0.024$, $Ce_2C_4^+ = 0.028$, $Ce_2C_5^+ = 0.024$, and $Ce_2C_6^+ = 0.023$, all in atm A^{-1} K^{-1}.

Results

Evaluation of Thermal Functions. The Gibbs energy functions needed for the evaluation of the various third-law enthalpies were taken from Hultgren et al.[17] for the species Ce(g) and C(s). The necessary thermal functions for the gaseous species Ce_2C_n, where n = 1-6, were calculated by using molecular parameters that were estimated along similar assumptions as those employed for the CeC_n species, where n = 1-6.[5]

Table II. Calculated Vibrational Frequencies

carbide	structure	freq, cm^{-1}
Ce_2C	A	1271, 643, 398 (2)
Ce_2C_2	A	1822, 979, 262, 714 (2), 194 (2)
Ce_2C_3	A	1839, 1432, 808, 234, 782 (2), 428 (2), 113 (2)
	B	1823, 998, 878, 256, 730 (2), 276 (2), 127 (2)
Ce_2C_4	A	1899, 1665, 1237, 695, 213, 834 (2), 587 (2), 289 (2), 77 (2)
	B	1843, 1787, 974, 685, 252, 731 (2), 552 (2), 244 (2), 83 (2)
Ce_2C_5	A	1926, 1784, 1500, 1088, 611, 197, 862 (2), 684 (2), 440 (2), 208 (2), 56 (2)
	B	1844, 1788, 995, 877, 685, 246, 745 (2), 553 (2), 304 (2), 155 (2), 77 (2)
Ce_2C_6	A	1939, 1847, 1656, 1357, 971, 547, 184, 879 (2), 745 (2), 550 (2), 338 (2), 157 (2), 43 (2)
	B	1854, 1810, 1775, 970, 685, 685, 241, 746 (2), 558 (2), 547 (2), 281 (2), 113 (2), 66 (2)

Linear structures for the Ce_2C_n molecules were assumed for all of the polyatomic species, because linear structures on the whole were shown to be preferred over assumed nonlinear structures for the molecule CeC_n.[5b] The structure Ce–C–Ce was assumed for the monocarbide. The similarity of M–C_2 bonding to M–O bonding, originally suggested by Chupka et al.,[18] has now been established for a large number of transition-metal dicarbides. Accordingly, a linear structure, Ce–C–C–Ce, was considered for the dicerium dicarbide. Linear structures of the configurations C–Ce–C–C–Ce and Ce–C–C–C–Ce were assumed for the dicerium tricarbide. Similarly, structures of the type C–C–Ce–C–C–Ce, Ce–C–C–C–C–Ce, C–C–Ce–C–C–Ce–C, Ce–C–C–C–C–C–Ce, C–C–Ce–C–C–Ce–C–C, and Ce–C–C–C–C–C–C–Ce were assumed for the gaseous dicerium tetra-, penta-, and hexacarbides, respectively. The structure for each molecule, Ce_2C_n ($n \geq 3$), that contains only one carbon chain and in which the cerium atoms are bonded at either end of the chain will be referred to as structure A in our discussion. The other structure, containing

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Table III. Evaluated Thermal Functions for the Gaseous Dicerium Carbide Molecules, Ce_2C_n (n = 1-6)

		temp, K									
		structure A					structure B				
species		298	2500	2600	2700	2800	298	2500	2600	2700	2800
Ce_2C	GEF	239.8	347.3	349.9	352.3	354.7					
	HCF	10.72									
Ce_2C_2	GEF	265.9	405.6	408.9	412.2	415.4					
	HCF	13.58									
Ce_2C_3	GEF	279.4	449.8	454.0	458.1	462.0	283.2	459.0	463.2	467.3	471.3
	HCF	15.91					16.69				
Ce_2C_4	GEF	292.2	492.1	497.0	501.9	506.5	292.8	496.6	501.6	506.4	511.1
	HCF	18.08					18.53				
Ce_2C_5	GEF	305.0	534.3	540.1	545.7	551.1	304.3	544.2	550.1	555.8	561.3
	HCF	20.25					21.65				
Ce_2C_6	GEF	317.8	576.5	583.1	589.4	595.6	308.2	576.1	582.7	589.2	595.4
	HCF	22.43					23.49				

Table IV. Reaction Enthalpies for the Reaction $Ce_2C_n(g) = 2Ce(g) + nC(graph)$, Standard Heats of Formation, Atomization Energies, and Other Thermochemical Data of the Gaseous Dicerium Carbides (kJ mol^{-1})

molecule	ΔH°_0[a]	ΔH°_{298}	$\Delta H_f{}^\circ_{298}$	$\Delta H_a{}^\circ_0$	$\Delta H_a{}^\circ_{298}$	$\Delta H_a{}^\circ_0$-(Ce_2C_n) − $\Delta H_a{}^\circ_0$-(CeC_n)	$\Delta H_a{}^\circ_0$-(Ce_2C_n) − $\Delta H_a{}^\circ_0$-(C_n)
Ce_2C	336 ± 4	339	506 ± 26	1047 ± 26	1056	606	1047
Ce_2C_2	268 ± 7	269	576 ± 25	1690 ± 25	1702	422	1094
Ce_2C_3							
structure A	224 ± 1	224		2358 ± 28	2374		
structure B	198 ± 1	198	647 ± 28	2332 ± 28	2348	499	1037
Ce_2C_4							
structure A	243 ± 9.0	243		3088 ± 25	3110		
structure B	231 ± 8.6	230	615 ± 25	3076 ± 25	3097	564	1248
Ce_2C_5							
structure A	126 ± 9	125		3682 ± 32	3709		
structure B	98 ± 9	95	750 ± 32	3654 ± 32	3679	543	1135
Ce_2C_6							
structure A	78 ± 4	76		4345 ± 36	4376		
structure B	79 ± 4	75	770 ± 36	4346 ± 36	4375	598	1345

[a] Errors correspond to standard; the uncertainties shown for $\Delta H_a{}^\circ_0$ and $\Delta H_f{}^\circ_{298}$ are estimated overall errors.

either C_2 or C units, will be referred to as structure B.

In the calculation of the various molecular vibrational frequencies and moments of inertia for the different Ce_2C_n molecules, the parameters employed in the previous report on monocerium carbides[5b,19-23] were used, and the reader is referred there. The calculations were performed by using an available modification of a Schachtschneider computer program.[24] The resulting vibrational frequencies are listed in Table II.

Following the procedure as employed by Balducci et al.[22] and ourselves[5] for the CeC_n molecules, the electronic contribution to the partition function of the different molecules was taken as that of Ce^{2+}.[25] We employed the even parity levels from the $4f^2[^3H_4]$ to the configuration $5d^2[^3F_2]$, and the odd parity levels from a configuration $f4d[^1G_4]$ to the level of the configuration $4f6s[(^2F_{5/2})s_{1/2}]$. These levels were employed because it was observed that any simple ground-state assumption alone was significantly inadequate in evaluating the different enthalpies of reactions. An improvement in the statistical error of evaluated third-law values of approximately 10% was observed employing these electronic levels.

When all the above assumptions were employed, the Gibbs free energy and heat content functions for the various molecules under discussion were computed by using standard statistical thermodynamic relations.[26] These values are listed in Table III.

Evaluation of Thermodynamic Properties. **Ce_2C_4.** The equilibrium reaction considered in the evaluation of the atomization energy for Ce_2C_4 was

$$Ce_2C_4(g) = 2Ce(g) + 4C(graph)$$

The evaluated third-law enthalpy for this reaction was calculated as $\Delta H^\circ_0 = 243 \pm 9.0$ ($\Delta H^\circ_{298} = 243$) kJ mol^{-1} for structure A and $\Delta H^\circ_0 = 231 \pm 8.6$ ($\Delta H^\circ_{298} = 230$) kJ mol^{-1} for structure B. These values are tabulated in Table IV.

We have measured over a significant temperature range (2589–2784 K) and reported a reasonable number of data sets (17 sets), but we can place no major significance on any evaluated second-law enthalpy. This was due to the fact that many of the evaluated data were measured at the same temperature, due to a changing Ce^+ ion intensity. Therefore, we must rely on only the third-law evaluation in determining the atomization energy of the molecule $Ce_2C_4(g)$.

The above third-law enthalpies yielded atomization energies, $\Delta H_a{}^\circ_0$ in kJ mol^{-1}, for the assumed structures A and B of 3088 ± 25 ($\Delta H_a{}^\circ_{298} = 3110$) and 3076 ± 25 ($\Delta H_a{}^\circ_{298} = 3097$),

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(19) Huber, K. P.; Herzberg, G. "Molecular Spectra and Molecular Structure"; Van Nostrand Reinhold Co.: New York, 1979; Vol. IV.

(20) Estimated from a relationship of γ_e for the molecule C_3 (Douglas, A. E. *Astrophys. J.* **1951**, *144*, 466) and a γ_e for the molecule C_3^- as compared with the ratio of experimental γ_e of C_2/C_2^-.

(21) The force constant was estimated from force constants of transition-metal monoxides having similar dissociation energies according to previously published results of CeC, such as MoO and CrO.

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respectively, by employing a value of 711.2 ± 2.1 kJ mol^{-1} ($\Delta H_v°_{298}$ = 716.7) for the reaction C(graph) = C(g).[17] The error limit of ±25 kJ mol^{-1} given for the atomization energy has been based on an estimated uncertainty of ±25% in the K_p values, ±15 K in the temperature and ±8 J K^{-1} mol^{-1} in the Gibbs energy functions. We recommend the value evaluated from assuming structure B (C–C–Ce–C–C–Ce) as the preferred atomization energy. As the various estimated molecular parameters differ from the unknown true value, a trend is developed with temperature within the calculated Gibbs energy functions. The greater the trend becomes the larger the standard deviation in the calculated third-law enthalpies. One observes the smallest standard deviation in structure B.

The standard heat of formation, $\Delta H_f°_{298}$, of Ce_2C_4(g) assuming structure B was derived as 615 ± 25 kJ mol^{-1}, by using the literature value for the heat of formation, $\Delta H_f°_{298}$[Ce(g)] = 422.6 ± 12.6 kJ mol^{-1},[17] and the evaluated third-law enthalpies.

Ce_2C_2. The Ce_2C_2 molecule was measured for only seven data sets and at low ion intensities, but was positively identified by its shutter effect, m/e ratio, and isotopic distribution. Also, the low measured upper limit for the appearance potential of ≤7.0 ± 2.0 eV supports this positive identification. The third-law enthalpy, $\Delta \mathrm{H}°_0$, of the reaction

$$Ce_2C_2(g) = 2Ce(g) + 2C(graph)$$

was determined as 268 ± 7 ($\Delta H°_{298}$ = 269) kJ mol^{-1}. The error term listed here represents the standard deviation.

This third-law value, in combination with the sublimation energy of C(graph),[17] gives the atomization energy of Ce_2C_2 as $\Delta H_a°_0$ = 1690 ± 25 kJ mol^{-1} ($\Delta H_a°_{298}$ = 1702 kJ mol^{-1}). This selected value of the atomization energy has an error limit of ± 25 kJ mol^{-1} based upon an estimated uncertainty of ± 30% in the K_p value, ±15 K in temperature, and a possible error in the calculated Gibbs energy function of ±8 J K^{-1} mol^{-1}.

The standard heat of formation, $\Delta H_f°_{298}$, for the gaseous Ce_2C_2 has been calculated from the third-law reaction enthalpy and the sublimation enthalpy of Ce(s)[17] as for the molecule Ce_2C_4. The resulting value is $\Delta H_f°_{298}$ = 576 ± 25 kJ mol^{-1}.

Ce_2C, Ce_2C_3, Ce_2C_5, and Ce_2C_6. The third-law enthalpy of reactions for the gaseous molecule Ce_2C was measured for the reaction

$$Ce_2C(g) = 2Ce(g) + C(graph)$$

An average third-law value of $\Delta H°_0$ = 336 ± 4 ($\Delta H°_{298}$ = 339) kJ mol^{-1} was determined.

The heat of atomization, $\Delta H_a°_0$, of Ce_2C gas has been evaluated as 1047 ± 20 ($\Delta H_a°_{298}$ = 1056) kJ mol^{-1}. This was done by utilizing the above calculated third-law enthalpy and the heat of sublimation of C(graph) taken from Hultgren et al.[17] The error limit associated with the dissociation energy is an estimated error considering possible error contributions similar to those listed for Ce_2Ce_4 and Ce_2C_2 but assuming a 40% error in the K_p value.

The equilibrium reactions considered in the analysis of the third-law enthalpies of the remaining dicerium carbides are as follows:

$$Ce_2C_3(g) = 2Ce(g) + 3C(graph) \quad (1)$$

$$Ce_2C_5(g) = 2Ce(g) + 5C(graph) \quad (2)$$

$$Ce_2C_6(g) = 2Ce(g) + 6C(graph) \quad (3)$$

The third-law enthalpies, $\Delta H°_0$, in kJ mol^{-1} were determined for reactions 1–3. These values are 224 ± 1 ($\Delta H°_{298}$ = 224) kJ mol^{-1} for structure A and 198 ± 1 kJ mol^{-1} ($\Delta H°_{298}$ = 198) for structure B by employing reaction 1. For reaction 2, the evaluated enthalpies were obtained as 126 ± 7 ($\Delta H°_{298}$ = 125) kJ mol^{-1} for structure A and 98 ± 7 ($\Delta H°_{298}$ = 76) kJ mol^{-1} for structure B. Finally for reaction 3, an enthalpy of 78 ± 7 kJ mol^{-1} ($\Delta H°_{298}$ = 76) for structure A and for structure B a value of 79 ± 3 ($\Delta H°_{298}$ = 75) kJ mol^{-1} are reported. The error terms represent the standard deviations.

Neither of the two structure models considered for the molecules Ce_2C_3(g), Ce_2C_5(g), and Ce_2C_6(g) are indicated to be more favorable from a thermodynamic consideration, on the basis of our estimated internal parameters. We thus propose that structure B be used for further evaluations, mainly because this structure is indicated by the bond additivitiy rule to be slightly more stable than structure A. Also, from an earlier report[5b] we noticed that the two predominent species CeC_2 (g) and CeC_4(g) probably have the structures Ce–C–C and C–C–Ce–C–C. This is due primarily to the increased stability of the C_2 negative ion.

Calculated atomization energies, $\Delta H_a°_0$, for the structure B of each gaseous molecule was obtained as 2332 ± 28 ($\Delta H_a°_{298}$ = 2348) kJ mol^{-1} for Ce_2C_3, 3654 ± 32 ($\Delta H_a°_{298}$ = 3679) kJ mol^{-1} for $Ce_2C_{5(g)}$, and 4347 ± 36 ($\Delta H_a°_{298}$ = 4375) kJ mol^{-1} for Ce_2C_6. Here, the error term corresponds to an estimated uncertainty assuming all possible errors, similar to Ce_2C but with an increasing unceertainty in Gibbs energy function with molecular size.

Standard heats of formation, H_{298}, for these four gaseous molecules were derived as 510 ± 26, 647 ± 28, 748 ± 32, and 766 ± 36 kJ mol^{-1} for Ce_2C, Ce_2C_3, Ce_2C_6, and CeC, respectively. The literature sublimation energy of cerium,[17] $H_{s,298}$ = 422.7 ± 12.6 kJ mol^{-1}, was used in obtaining these values.

Summary and Discussion

The various data reported in the early part of this paper are summarized in Table IV. The data include the reaction enthalpies, $\Delta H°_0$ and $\Delta H°_{298}$, for

$$Ce_2C_n(g) = Ce(g) + nC(s)$$

at both 0 K and 298 K, evaluated atomization energies, $\Delta H_a°_0$ and $\Delta H_a°_{298}$, at both 0 K and 298 K, the standard heat of formation, $\Delta H_f°_{298}$, and other thermodynamic correlations. The values represented here are different than preliminary values reported previously.[3,5a,36] The present values represent primarily a change in the estimated vibrational parameters, particularly in the bending force constants and the assumed bond distance of C_2 units. The present parameters employed reflect more accurately the most recent published data on this diatomic molecule.

We have chosen the preferred structure B in the earlier evaluations. As seen from Table IV, the enthalpy difference between structures A and B in all cases is less than 30 kJ mol^{-1}, even as low as 1 kJ mol^{-1} for the molecule Ce_2C_6. Also, the bond additivity has been shown[7c,33] to aid in determining preferred structures due to an increase in stability of one structure over another. The atomization energies are obtained by adding the M–C_n and C_n bond energies in the individual molecules. The resulting difference (not listed) between the different structures is less than or equal to any uncertainty one may be able to assign to the evaluated values, favoring only structure B slightly. We also assumed this structure from a slightly lower standard deviation in the third-law evaluation of the reaction

$$CeC_4(g) = 2Ce(g) + 4C(graph)$$

This difference may not be significant.

Chupka et al.,[18] through their pioneering work on vaporization behavior of metal carbides, pointed out the pseudooxygen character of the C_2^- group. DeMaria and various co-workers[27-30] have extended this analogy to several different

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rare-earth carbides and extended it to encompass the tetracarbides. Kohl and Stearns[31,32] have found this analogy to be applicable to all group 3B and 4B transition-metal di- and tetracarbides. The energy difference between the M–O and $M-C_2$ bonds may be interpreted as arising from a difference in electronegativity of O and C_2 radicals of 3.5 and 3.3, respectively, on the Pauling scale.[13]

The authors in another paper[5b] have extended these empirical correlations to a more general explanation of the structures of $CeC_n(g)$ molecules. The significant stability of the C_2 negative ion compared to negative ions of higher carbon chains is supported by molecular orbital considerations.[34,35] Thus a structure that contains only two small carbon fragments may be a strong possibility as a preferred structure of the numerous Ce_2C_n gaseous molecules. Our evidence for this assumption is very marginal. The only certainty that can be said about these molecules is that the metal atoms are not bonded together.

The latter statement can be supported by the difference $\Delta H_a{}^\circ{}_0\,(Ce_2C_n) - \Delta H_a{}^\circ{}_0\,(CeC_n)$, Table IV. This difference represents the bond dissociation of the second cerium metal atom. The value of the difference increases with increasing C_n size (except in the case of Ce_2C). These values are approximately equal to the corresponding bond dissociation of the monocerium carbides, CeC_n.

Also the difference $\Delta H^\circ{}_0(Ce_2C_n) - \Delta H^\circ{}_0(C_n)$, which is approximately 1200 kJ mol^{-1}, is significantly higher than the reported dissociation energy of Ce_2, $D^\circ{}_0 = 238 \pm 21$ kJ mol^{-1},[3] thereby implying strongly that the Ce–Ce bond is not contained within the molecule.

The results and discussion presented in the present paper amply demonstrate the very complex nature of the vapors of transition-metal carbides. If a stable dicarbide exists [$D^\circ{}_0(M-C_2)$ 600 kJ mol^{-1}], one will observe a whole series of species of the types MC_n and M_2C_n at high enough temperatures. While we have suggested choices in predicting structures, there is very little information available with which to accurately estimate the various partition functions. Therefore we hope that this discussion will stimulate theoretical and optical spectroscopic investigations that can be expected to enhance the knowledge of the molecular and electronic structure and of the nature of bonding in these types of molecules.

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Registry No. Ce, 7440-45-1; Ce_2C, 58591-86-9; Ce_2C_2, 12011-58-4; Ce_2C_3, 12115-63-8; Ce_2C_4, 12012-32-7; Ce_2C_5, 58591-83-6; Ce_2C_6, 39461-15-9; graphite, 7782-42-5.

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Electron Self-Exchange by Hexakis(cyclohexyl isocyanide)manganese(I/II): Solvent, Electrolyte, and Temperature Dependences[1]

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The rate of electron self-exchange between MnL_6BF_4 and $MnL_6(BF_4)_2$ (L is CNC_6H_{11}) has been measured by ^{55}Mn NMR line broadening as a function of reactant concentration, solvent, added electrolyte, and temperature. Ion association between the manganese complexes and BF_4^- has been measured by conductivity. The second-order rate constants at 26 °C and the activation parameters in the presence of 0.08 M tetrabutylammonium tetrafluoroborate are as follows ($10^{-5}k$ in M^{-1} s^{-1}, $\Delta H^\ddagger$ in kcal/mol, $\Delta S^\ddagger$ in cal/(mol deg)): dimethyl sulfoxide, 10.8 ± 0.6, 3.5 ± 1.5, −19 ± 5; acetonitrile, 4.38 ± 0.07, 3.4 ± 0.1, −21 ± 1; ethanol, 2.51 ± 0.02, 3.5 ± 0.1, −22 ± 1; acetone, 2.51 ± 0.04, 3.5 ± 0.1, −22 ± 1; bromobenzene, 0.961 ± 0.001, 6.0 ± 0.1, 15 ± 1; chloroform, 0.585 ± 0.006, 4.3 ± 0.1, −22 ± 1. The dependence of the rate constants on added electrolyte varied with the solvent, increasing with added salt in the more polar solvents and decreasing in the less polar solvents. This has been interpreted in terms of electrostatic work in forming the precursor complex and inhibition by ion association. The rate constants for the various paths in the different solvents have been resolved by using the kinetic and conductivity data. The solvent dependence of these rate constants is opposite in sign to that predicted, by using dielectric continuum theory for the solvent reorganization, within Marcus' theory for outer-sphere electron transfer.

Introduction

Recent research activity in the field of electron-transfer reactions has involved refinement of the theoretical models and extension and refinement of experimental measurements in a cooperative manner.[2-5] This has lead to significant progress in an area that has long been an active one. In our laboratory we are pursuing detailed studies of well-defined outer-sphere electron-transfer systems in order to assess the influence of solvent, ion pairing, and variation of the size of the complexes on electron-transfer efficiency and to compare the results with the predictions of current theories.[6,7] Relatively little work has been done on electron transfer by substitution-inert transition-metal complexes in nonaqueous solvents, but those

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