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Gas-Phase Reactions of La^{2+} with Small Alkanes and the Photodissociation of $LaC_2H_4^{n+}$ and $LaC_3H_6^{n+}$ (n = 1 and 2)

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Abstract: The gas-phase reactivity of La^{2+} with C_1–C_4 linear alkanes is investigated and compared to the analogous reactions of La^+. La^{2+} is unreactive with methane and ethane but reacts with propane and butane to give dehydrogenation, alkane loss, and for butane charge-splitting reaction products. Interestingly, charge transfer is not observed in agreement with a simple curve-crossing model. Four ligated species, namely, $LaC_2H_4^+$, $LaC_2H_4^{2+}$, $LaC_3H_6^+$, and $LaC_3H_6^{2+}$, are photodissociated and the photodissociation thresholds are used directly, or together with information from ligand displacement reactions, to assign thermochemical values for these processes and metal ligand bond energies. The bonding properties of $LaC_2H_2^+$ and $LaC_2H_2^{2+}$ are also investigated. A surprising outcome of this study is that the monocation is in some cases more strongly bound to these ligands than the dication. Theoretical calculations by Bauschlicher and co-workers are in good agreement with these results.

Introduction

The gas-phase chemistry of singly-charged atomic transition-metal ions, ion complexes, and small metal cluster ions has been an area of considerable interest for several years.[1] These studies yield information applicable to a diverse range of subjects from atmospheric chemistry to providing simplified models for reactions occurring on surfaces. In addition, the absence of a solvent allows the "intrinsic" chemistry of the species to be probed, and the effect of one ligand in the presence or absence of more ligands can also be studied. These gas-phase studies have furnished a wealth of mechanistic, kinetic, and thermochemical information. Research involving the gas-phase chemistry of doubly-charged transition-metal ions, however, is still in its infancy.

One reason for the lack of research on multiply-charged ions in the gas phase is that the second ionization potentials of metals are generally higher than the first ionization potentials of most organic molecules.[2] This fact would lead one to believe that the only primary reaction pathway available to gas-phase multiply-charged metal cations is charge exchange. However, flowing afterglow studies performed by Tonkyn and Weisshaar on the reactivity of Ti^{2+} with methane, ethane, and propane showed that, although charge exchange and charge splitting reactions are observed, they are not the only reaction pathways available to Ti^{2+}.[3] Soon after the initial paper by Tonkyn and Weisshaar, our laboratory reported on the reactions of Nb^{2+} with methane where, again, the main reaction pathway was not charge exchange but the formation of $NbCH_2^{2+}$ at approximately 52% yield.[4] Since then, we have reported on the reactions of Nb^{2+}, $LaFe^{2+}$, Zr^{2+}, Ta^{2+}, and Y^{2+} with small alkanes.[5] Here we extend our study of doubly-charged metal cations to the reactivity of La^{2+}.

The second ionization potential of lanthanum is only 11.06 eV,[2] which is lower than the ionization potentials of methane and ethane. Thus, it was expected that the reactivity of La^{2+} would lead to less charge exchange than for all of the above metal ions, which have considerably higher second ionization potentials, and that possibly this would open up interesting reaction channels inaccessible to these other metals. In addition, La^{2+} has only one valence electron and, therefore, cannot react via the usual oxidative addition pathway to form two covalent bonds. We have begun to investigate such low-valence systems.[6]

A survey of the photochemistry of $LaC_2H_4^{2+}$ and $LaC_3H_6^{2+}$ generated in this study revealed that, like their singly-charged analogues, these ions readily photodissociate. This provided the opportunity to compare for the first time the photofragments generated from a doubly-charged metal ion species and its singly-charged counterpart. The singly-charged ethene ion was prepared from the reaction with ethane, while the doubly-charged ethene and the singly- and doubly-charged propene ions were prepared from propane. Threshold photodissociation measurements along with ligand displacement reaction studies permitted a direct comparison of the bond energies of the singly- and doubly-charged species. Surprisingly, in some cases $D°(La^+–L)$ is found to be greater than $D°(La^{2+}–L)$. These results spawned a detailed theoretical treatment by Bauschlicher and co-workers, and some of their findings are discussed briefly.

Experimental Section

The theory, instrumentation, and methodology of Fourier transform mass spectrometry (FTMS) have been discussed elsewhere.[7] All experiments were performed on a prototype FTMS-1000 or an FTMS-2000 instrument, both from Nicolet and each equipped with a Nd:YAG laser. Singly- and doubly-charged lanthanum cations were generated by focusing the fundamental frequency (1064 nm) of the laser onto a high-purity block of lanthanum metal.[8] A stable La^{2+} signal was achieved by operating the laser power just above threshold for ion formation and continuously ejecting the singly-charged ion for the first 5 ms following the laser pulse. The FTMS-1000 has a 5.2-cm cubic cell situated between the poles of a Varian 15-in. electromagnet maintained at around 0.85 T. The two transmitter plates have been replaced with 80% transmittance stainless steel screens which allow light from a 2.5 kW Hg–Xe arc lamp to irradiate the ions during photodissociation experiments. Photodissociation thresholds were determined using cutoff filters characterized on a UV–vis spectrometer and the filter cutoffs were assigned at approximately 1% transmittance. In addition, the thresholds observed are assumed to arise from single-photon processes. All chemicals were either leaked into the cell through Varian leak valves in order to maintain a constant background pressure or pulsed into the cell using General Valve Corp. series 9 pulsed solenoid valves.[9] The pulse profile was such that the pressure peaked at about 150 ms after firing the valve and was pumped away in about 500 ms. All samples were used as supplied except for multiple freeze–pump–thaw cycles to remove any non-condensible gases. Pressures were measured with an uncalibrated

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Table I. Primary Product Ion Abundances of the Reactions of La^+ and La^{2+} with Simple Linear Alkanes

		La^+		La^{2+}	
	neutral loss	ion	%	ion	%
methane		no reaction		no reaction	
ethane	H_2	$LaC_2H_4^+$	100	no reaction	
propane	H_2	$LaC_3H_6^+$	85	$LaC_3H_6^{2+}$	81
	$2H_2$	$LaC_3H_4^+$	15		
	CH_4			$LaC_2H_4^{2+}$	19
butane	H_2	$LaC_4H_8^+$	4	$LaC_4H_8^{2+}$	38
	$2H_2$	$LaC_4H_6^+$	77	$LaC_4H_6^{2+}$	11
	C_2H_4	$LaC_2H_6^+$	19		
	C_2H_6			$LaC_2H_4^{2+}$	34
	CH_4			$LaC_3H_6^{2+}$	6
				$LaCH_3^+ + C_3H_7^+$	8
				$LaH^+ + C_4H_9^+$	3

Bayard-Alpert ionization gauge. Collision-induced dissociation (CID) was performed as previously described[10] and Ar was used as the collision gas at a total pressure of about 1×10^{-5} Torr. The collision energy of the ions can be varied typically between 0 and 150 eV in the laboratory frame. To ensure that all of the reactions studied were thermal, the ions were allowed to collide with Ar at approximately 1×10^{-5} Torr for from 500 ms to 1 s. This allowed the ions to undergo approximately 100–400 thermalizing collisions.[11] At the end of this time, all ions were ejected from the cell by typical ejection pulses except for the ion to be studied.[12] The percent ion intensities were obtained in all cases from the metal-containing product ion species.

Results and Discussion

Reaction Chemistry. The reaction products of singly- and doubly-charged lanthanum with alkanes up to butane are given in Table I for comparison. Doubly-charged lanthanum, like singly-charged lanthanum, does not react with methane via any observable bimolecular pathway at thermal energies.[13] The fact that no charge exchange is seen is consistent with the ionization potential of methane (12.5 eV) being higher than the second ionization potential of lanthanum (11.06 eV).[2] Interestingly, La^{2+} is also unreactive with ethane, and the lack of charge exchange products is gratifying in that the ionization potential of ethane (11.52 eV)[2] is only about 0.5 eV higher than the second ionization potential for lanthanum. Thus, this once again indicates that the La^{2+} ions are not appreciably excited.

La^{2+} reacts with propane by dehydrogenation and demethanation, reactions 1 and 2. $LaC_2H_4^{2+}$ produced by demethanation reacts further with propane by displacement as shown in reaction 3. This latter reaction has also been observed for $YC_2H_4^{2+}$ and is consistent with theoretical calculations that indicate that propane binds more strongly to Y^{2+} than ethylene.[14]

$$\mathrm{La^{2+} + C_3H_8 \longrightarrow LaC_3H_6^{2+} + H_2} \qquad 81\% \qquad (1)$$

$$\mathrm{\longrightarrow LaC_2H_4^{2+} + CH_4} \qquad 19\% \qquad (2)$$

$$\mathrm{LaC_2H_4^{2+} + C_3H_8 \longrightarrow LaC_3H_8^{2+} + C_2H_4} \qquad 100\% \qquad (3)$$

La^+ reacts with propane in a manner similar to La^{2+} to form $LaC_3H_6^+$ in about 85% abundance.[13] The doubly dehydrogenated product $LaC_3H_4^+$ is observed at 15% abundance. The fact that La^+ forms a doubly-dehydrogenated product while La^{2+} does not may be due to a higher reaction exothermicity for the La^+ than for La^{2+}. As discussed below, the bond energies determined for La^+ and La^{2+} support this supposition.

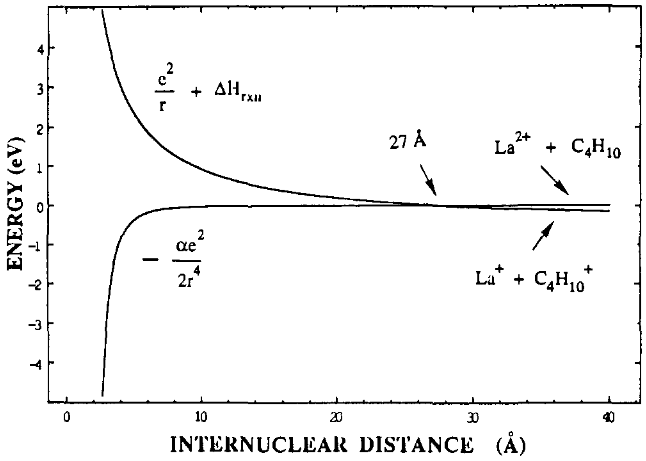

Figure 1. Charge exchange surface for the closest resonant electron hop between La^{2+} and butane.

Collision-induced dissociation (CID) has proved to be one of the most useful methods for ion structure determinations. CID of $LaC_2H_4^{2+}$ (reaction 4) and $LaC_3H_6^{2+}$ (reaction 5) yields La^{2+} exclusively over the entire energy range studied (0–150 eV), suggesting intact ligand structures.

$$\mathrm{LaC_2H_4^{2+} \xrightarrow{CID} La^{2+} + C_2H_4} \qquad (4)$$

$$\mathrm{LaC_3H_6^{2+} \xrightarrow{CID} La^{2+} + C_3H_6} \qquad (5)$$

La^{2+} reacts with *n*-butane to form a surprising number of products, as shown in reactions 6–11. These products are compared with those from the reaction of La^+ in Table I. There are two charge splitting processes observed for La^{2+}, reactions 9 and 10, and in analogy to the reaction with propane, $LaC_2H_4^{2+}$ reacts further with butane to displace the ethene in favor of the alkane, reaction 12. Two of the reaction pathways from the reaction of La^+ are analogous to that of La^{2+}, i.e. loss of H_2 and $2H_2$, but the absolute intensities of these two products are substantially different than for the doubly-charged species. In particular, the loss of $2H_2$ is again more prevalent than loss of H_2 for La^+ compared to La^{2+}.

$$\mathrm{La^{2+} + C_4H_{10} \longrightarrow LaC_4H_8^{2+} + H_2} \qquad 38\% \qquad (6)$$

$$\mathrm{\longrightarrow LaC_4H_6^{2+} + 2H_2} \qquad 11\% \qquad (7)$$

$$\mathrm{\longrightarrow LaC_2H_4^{2+} + C_2H_6} \qquad 34\% \qquad (8)$$

$$\mathrm{\longrightarrow LaCH_3^{+} + C_3H_7^{+}} \qquad 8\% \qquad (9)$$

$$\mathrm{\longrightarrow LaH^{+} + C_4H_9^{+}} \qquad 3\% \qquad (10)$$

$$\mathrm{\longrightarrow LaC_3H_6^{2+} + CH_4} \qquad 6\% \qquad (11)$$

$$\mathrm{LaC_2H_4^{2+} + C_4H_{10} \longrightarrow LaC_4H_{10}^{2+} + C_2H_4} \qquad 100\% \qquad (12)$$

Reactions with propane and butane do not give direct charge transfer even though the reactions are exothermic. Lindinger and co-workers measured the rates of charge transfer reactions and explained their observations by a simple model involving the crossing of potential energy surfaces.[15] As applied to the present work, one surface is the ion-induced dipole attraction between La^{2+} and the neutral ($-\alpha e^2/2r^4$) and the other is the Coulombic repulsion surface ($e^2/r + \Delta H_{rxn}$) between what would be the charge transfer products La^+ and N^+, where ΔH_{rxn} is the exothermicity of the charge transfer reaction and N is the neutral. The reaction window suggested by the authors for effective charge transfer is when the internuclear distance is between 2 and 6 Å, although

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Table II. Calculated Closest Approach for Resonant Electron and Anion Transfer with Various Hydrocarbons

$La^{2+} + N \rightarrow La^+ + N^+$

N	ΔH_{rxn} (eV)[a]	α (Å^3)[b]	r (Å)
CH_4	+1.45	2.60	none
C_2H_4	−0.56	4.25	25
C_2H_6	+0.46	4.44	none
C_3H_8	−0.11	6.29	131
C_3H_6	−1.33	6.07	11
C_4H_{10}	−0.53	8.14	27
C_5H_{12}	−0.71	9.98	20
C_6H_{14}	−0.93	11.83	16
C_7H_{16}	−1.14	13.68	13
C_8H_{18}	−1.20	15.52	12
C_9H_{20}	−1.34	17.37	11

$La^{2+} + C_4H_{10} \rightarrow LaX^{+c} + Y^+$

X^-	Y^+	ΔH_{rxn} (eV)	α (Å^3)	r (Å)
CH_3^-	$C_3H_7^+$	−1.60	8.14	9
H^-	$C_4H_9^+$	−1.30	8.14	11

[a] Ionization potentials and the heats of formation are from ref 2. [b] Polarizabilities were obtained from: Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206. Miller, K. *J. Am. Chem. Soc.* **1990**, *112*, 8533. Those for C_3H_6 are from: Maryott, A. A.; Buckley, F. U.S. National Bureau of Standards Circular No. 537, 1953. [c] Bond energies for LaX^+ were obtained from ref 21 and for a complete compilation of bond energy values refer to: Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

some charge transfer can be observed at distances near 10 Å.[16] Figure 1 shows the curve crossing for butane. In this simple picture, the closest distance a resonant electron hop can occur from butane to the La^{2+} is when the total heat of the reaction is incorporated into Coulombic repulsion which occurs at an internuclear distance of 27 Å. The distances calculated for propane and butane are far too great for effective charge transfer to occur and, thus, it is not observed. For this reason, charge transfer will not be observed unless the reaction is sufficiently exothermic (≤−1 eV), and this must be taken into account when performing bracketing experiments on multiply charged ions to obtain thermochemical limits.[16] Curve crossing points for several small hydrocarbons with La^{2+} are given in Table II.

Photodissociation Studies. Photodissociation has proved to be an effective method of obtaining structure and bond energy information on ionic species.[17] Photodissociation requires that an ion absorb a photon and that the photon energy exceeds the enthalpy of the dissociation process (assuming single photon absorption). A thermodynamic threshold can be obtained only if the ion absorbs in the same energy range as that required for the dissociation and if there is no significant potential energy barrier to dissociation. If the ion does not absorb in this energy region, however, a spectroscopic threshold is obtained instead, yielding an upper limit for the process. Fortunately, due to the high density of electronic energy levels associated with transition metals, in many cases photodissociation of metal-containing ions gives thermodynamic thresholds. These results also indicate that potential energy barriers in these processes are often negligible. With a view toward comparing the bond energies of singly- and doubly-charged lanthanum, $LaC_2H_4^+$ and $LaC_2H_4^{2+}$ were generated by reacting La^+ and La^{2+} with ethane and propane, respectively, and subsequently irradiated with the arc lamp. These species yield the photoproducts in reactions 13–16. Also listed are the corresponding photodissociation threshold energies obtained in this work as discussed below.

threshold, kcal/mol

$$LaC_2H_4^+ \xrightarrow{h\nu} La^+ + C_2H_4 \qquad <65 \qquad (13)$$

$$LaC_2H_4^{2+} \xrightarrow{h\nu} La^{2+} + C_2H_4 \qquad 45 \pm 5 \qquad (14)$$

$$\longrightarrow LaC_2H_2^{2+} + H_2 \qquad 42 \pm 5 \qquad (15)$$

$$\longrightarrow LaC_2H_3^{2+} + H \qquad 51 \pm 5 \qquad (16)$$

$LaC_2H_4^+$ photodissociates to lose ethylene, reaction 13. Unfortunately, due to the long trapping times required for these photodissociation experiments (~10 s), La^+ thus produced reacts with background oxygen (present inherently in the instrument and via sample introduction) to form oxides, preventing a clear threshold from being obtained. Therefore, only an upper limit of 65 kcal/mol for the bond energy is assigned based on where the photoappearance of La^+ is clearly observed. Displacement reactions, however, indicate $D°(La^+–C_2H_2) > D°(La^+–C_2H_4)$ and $D°(La^+–C_6H_6) > D°(La^+–C_2H_4)$. Direct photodissociation in this study yielded $D°(La^+–C_6H_6) = 55 \pm 5$ kcal/mol, in good agreement with an earlier value from this laboratory of $D°(La^+–C_6H_6) = 50 \pm 3$ kcal/mol also obtained from direct photodissociation measurements.[18] The shorter trapping times (1–3 s) required to observe photodissociation of $LaC_6H_6^+$ prevented oxide formation from interfering with obtaining a good photodissociation threshold. This gives an average value of 53 ± 6 kcal/mol for $D°(La^+–C_6H_6)$. Exothermic dehydrogenation of ethane by La^+ (Table I) indicates that $D°(La^+–C_2H_4) > 33$ kcal/mol. Taken together, these observations give a range of 33 kcal/mol $< D°(La^+–C_2H_4) < 53 \pm 6$ kcal/mol.

Figure 2 illustrates the photodisappearance of the $LaC_2H_4^{2+}$ parent ion and the appearance of the photoproducts. Charge splitting products such as La^+ and $C_2H_4^+$ are noticeably absent. This can be rationalized on the basis of the calculated curve crossing distance for ethylene of 25 Å (Table II), which is well beyond the reaction window. Unlike its singly charged counterpart, oxide formation did not pose a problem for the doubly charged ion. Assuming that the photodissociation thresholds are a good measure of the endothermicity of reactions 14–16, a point which is discussed below, and using supplementary thermochemical data,[2,19] the following bond energy values are obtained: $D°(La^{2+}–C_2H_4) = 42 \pm 5$ kcal/mol, $D°(La^{2+}–C_2H_2) = 42 \pm 7$ kcal/mol, and $D°(La^{2+}–C_2H_3) = 102 \pm 7$ kcal/mol. These and other bond energy values from this work are tabulated in Table III. In addition, related thermochemical data are listed in Table IV.

threshold, kcal/mol

$$LaC_3H_6^+ \xrightarrow{h\nu} LaC_3H_4^+ + H_2 \qquad <2\% \qquad (17)$$

$$\longrightarrow LaC_3H_2^+ + 2H_2 \qquad 52 \pm 5 \qquad (18)$$

$$\longrightarrow LaC_2H_2^+ + CH_4 \qquad 51 \pm 5 \qquad (19)$$

$$\longrightarrow LaCH_2^+ + C_2H_4 \qquad <2\% \qquad (20)$$

$$\longrightarrow La^+ + C_3H_6 \qquad <63 \qquad (21)$$

Photodissociation of $LaC_3H_6^+$ gives a number of product ions, reactions 17–21. $LaC_3H_4^+$, produced by H_2 loss, is also produced in the parent reaction between La^+ and C_3H_8 (Table I). This ion, which is ejected during the isolation of the parent ion, appears as a photodissociation product at very low intensity (<2%), and an accurate threshold for it could not be determined. Similarly, a low photodissociation cross section is observed for $LaCH_2^+$ in reaction 20 (<2%), which prevented its threshold from being determined reliably. Finally, due to the propensity of La^+ to form oxides, which interfered with measuring an exact threshold, only an upper limit for process 21 could be assigned.

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Table III. Comparison of Bond Energies (kcal/mol) Obtained by Several Methods

		direct[a] PDS	indirect from PDS	displacement or reaction	theory[b]	recommended value
$D°(La^+–C_2H_2)$		<65	32 ± 11[c]	53 ± 6	66	53 ± 6
$D°(La^{2+}–C_2H_2)$			42 ± 7[d]	≥42[f]	44	38 ± 10
			34 ± 7[e]			
$D°(La^+–C_2H_4)$		<65		$33^g \le x < 53 \pm 6$	46	43 ± 10
$D°(La^{2+}–C_2H_4)$		42 ± 5		≥23[h]	41	42 ± 5
$D°(La^+–C_3H_6)$		<63		$30^i \le x < 53 \pm 6$	51	51 ± 10
$D°(La^{2+}–C_3H_6)$		42 ± 5		≥30[j]	48	42 ± 5
$D°(La^{2+}–C_3H_5)$			85 ± 7[k]			85 ± 7
$D°(La^{2+}–C_3H_4)$	$CH_2{=}C{=}CH_2$		41 ± 7[l]			41 ± 7
	$CH_3{-}C{\equiv}CH$		40 ± 7[l]			40 ± 7
$D°(La^{2+}–C_3H_3)$			126 ± 7[m]			126 ± 7
$D°(La^{2+}–C_3H_2)$	$CH_2{=}C{=}C{:}$		123 ± 12[n]			123 ± 12
	$:CH{-}C{\equiv}C{-}H$		130 ± 12[n]			130 ± 12
$D°(La^{2+}–C_2H_3)$			102 ± 7[o]			99 ± 7
			96 ± 7[p]			

[a] Direct from the threshold energy of the process $ML^{n+} \rightarrow M^{n+} + L$. [b] Reference 20. [c] Using the threshold energy for reaction 19 and the recommended bond energy $D°(La^+–C_3H_6)$ = 51 ± 10 kcal/mol. [d] Using the threshold energy for reaction 15 and the recommended energy $D°(La^{2+}–C_2H_4)$ = 42 ± 5 kcal/mol. [e] Using the threshold energy for reaction 27 and the recommended bond energy $D°(La^{2+}–C_3H_6)$ = 42 ± 5 kcal/mol. [f] Exothermic dehydrogenation of ethylene by La^{2+}. [g] Exothermic dehydrogenation of ethane by La^+. [h] Exothermic deethanation of butane by La^{2+} (reaction 8). [i] Exothermic dehydrogenation of propane by La^+ (Table I). [j] Exothermic dehydrogenation of propane by La^{2+} (reaction 1). [k] Using the threshold energy for reaction 23 and recommended bond energy $D°(La^{2+}–C_3H_6)$ = 42 ± 5 kcal/mol. [l] Using the threshold energy for reaction 24 and recommended bond energy $D°(La^{2+}–C_3H_6)$ = 42 ± 5 kcal/mol. [m] Using the threshold energy for reaction 25 and recommended bond energy $D°(La^{2+}–C_3H_6)$ = 42 ± 5 kcal/mol. [n] Using the threshold energy for reaction 18 and the recommended bond energy $D°(La^+–C_3H_6)$ = 51 ± 10 kcal/mol and heats of formation from ref 28. [o] Using the threshold energy for reaction 16 and recommended bond energy $D°(La^{2+}–C_2H_4)$ = 42 ± 5 kcal/mol. [p] Using the threshold energy for reaction 26 and recommended bond energy $D°(La^{2+}–C_3H_6)$ = 42 ± 5 kcal/mol.

Table IV. Thermochemical Information Derived from the Results Obtained from Photodissociation and Displacement

value	kcal/mol
$\Delta H_f(LaC_3H_6^+)$	186 ± 10[a]
$\Delta H_f(LaC_3H_6^{2+})$	450 ± 5
$\Delta H_f(LaC_3H_5^{2+})$	441 ± 7
$\Delta H_f(LaC_3H_4^{2+})$	492 ± 7
$\Delta H_f(LaC_3H_3^{2+})$	443 ± 7
$\Delta H_f(LaC_3H_2^+)$	238 ± 11[a]
$\Delta H_f(LaC_2H_3^{2+})$	457 ± 7[b] (463 ± 7)[c]
$\Delta H_f(LaC_2H_2^+)$	234 ± 6[d]
$\Delta H_f(LaC_2H_2^{2+})$	500 ± 7[e] (508 ± 7)[f]
$\Delta H_f(LaC_2H_4^{2+})$	458 ± 5
$\Delta H_f(LaC_2H_4^+)$	205 ± 10[g]
2nd I.P. (LaC_2H_2)	266 ± 9 (11.5 eV)[e]
	276 ± 9 (11.9 eV)[f]

[a] Calculated using $D°(La^+–C_3H_6)$ = 51 ± 10 kcal/mol. [b] Calculations from reaction 16. [c] Calculations from reaction 26. [d] Calculated using $D°(La^+–C_2H_2)$ = 53 ± 6 kcal/mol. [e] Calculations from reaction 15. [f] Calculations from reaction 27. [g] Calculated using $D°(La^+–C_2H_4)$ = 40 ± 10 kcal/mol.

Ligand displacement reactions were carried out to obtain additional information about $D°(La^+–C_3H_6)$. When $LaC_3H_6^+$ is reacted with benzene, the C_3H_6 ligand is displaced to yield $LaC_6H_6^+$. Since the reverse reaction is not observed, we conclude that $D°(La^+–C_3H_6) < D°(La^+–C_6H_6) = 53 \pm 6$ kcal/mol, suggesting that the direct photodissociation threshold $D°(La^+–C_3H_6)$ < 63 kcal/mol (reaction 21) is in fact only an upper limit. The ligand displacement and photodissociation results indicate that the theoretical value of 51 kcal/mol[20] is reasonable and, therefore, it is assigned as the correct value for the $D°(La^+–C_3H_6)$ bond energy. Another case where the bond energy from direct photodissociation needed verification by displacement reactions was for $LaC_2H_2^+$. An upper limit of 65 kcal/mol was obtained from reaction 22 instead of a definite threshold, due to the same

threshold, kcal/mol

$$LaC_2H_2^+ \xrightarrow{h\nu} La^+ + C_2H_2 \qquad <65 \tag{22}$$

problems encountered with $LaC_3H_6^+$. The threshold for reaction 19 gives $D°(La^+–C_2H_2)$ = 32 ± 11 kcal/mol, however, which is probably too low. One possibility is that the threshold obtained for reaction 19 is a spectroscopic and not a thermodynamic threshold, in which case the calculated bond energy for $D°(La^+–C_2H_2)$ would be lower than expected. Ligand displacement reactions were run, therefore, to try to bracket the bond energy. $LaC_2H_2^+$ is observed to react with benzene to displace acetylene, but the reverse reaction in which $LaC_6H_6^+$ reacts with acetylene to displace benzene is also observed. The rate in both directions appears to be on the same order of magnitude, suggesting that $D°(La^+–C_2H_2) \approx D°(La^+–C_6H_6) = 53 \pm 6$. Competitive CID studies on the mixed complex, $La(C_2H_2)(C_6H_6)^+$, at 15 eV of laboratory energy yield about equal loss of C_2H_2 and C_6H_6, in accordance with the displacement reactions. Thus, we assign $D°(La^+–C_2H_2)$ = 53 ± 6 kcal/mol and believe that the threshold from reaction 19 is spectroscopic. This value, however, is considerably lower than a limit of >65 kcal/mol obtained from an ion-beam study.[21]

The photodissociation processes observed for $LaC_3H_6^{2+}$ are shown in reactions 23–28. Interestingly, photodissociation yields substantial H and CH_3 loss, as is also observed for the photodissociation of $YC_3H_6^{2+}$.[22] The loss of radicals is not seen in the

threshold, kcal/mol

$$LaC_3H_6^{2+} \longrightarrow LaC_3H_5^{2+} + H \qquad 43 \pm 5 \tag{23}$$

$$\longrightarrow LaC_3H_4^{2+} + H_2 \qquad 42 \pm 5 \tag{24}$$

$$\longrightarrow LaC_3H_3^{2+} + H_2 + H \qquad 45 \pm 5 \tag{25}$$

$$\longrightarrow LaC_2H_3^{2+} + CH_3 \qquad 48 \pm 5 \tag{26}$$

$$\longrightarrow LaC_2H_2^{2+} + CH_4 \qquad 40 \pm 5 \tag{27}$$

$$\longrightarrow La^{2+} + C_3H_6 \qquad 42 \pm 5 \tag{28}$$

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(21) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845. Their value of $D°(La^+–C_2H_2)$ is based on the apparent observation of $La^+ + C_2H_6 \rightarrow La(C_2H_2)^+ + 2H_2$. We have found, however, that the presence of trace amounts of ethylene, e.g., > 0.1%, commonly found in a chemically pure lecture bottle of ethane is sufficient to produce observable intensities of $LaC_2H_2^+$. A GC analysis showed 0.6–0.7% contamination in our sample of ethane. Armentrout and Sunderlin have informed us that about 0.8% ethene must be present to reproduce the beam results assuming the reaction goes at the collision limit. As further proof of our results, $LaC_2H_2^+$, was not observed in the absence of C_2H_4 (<0.1%).

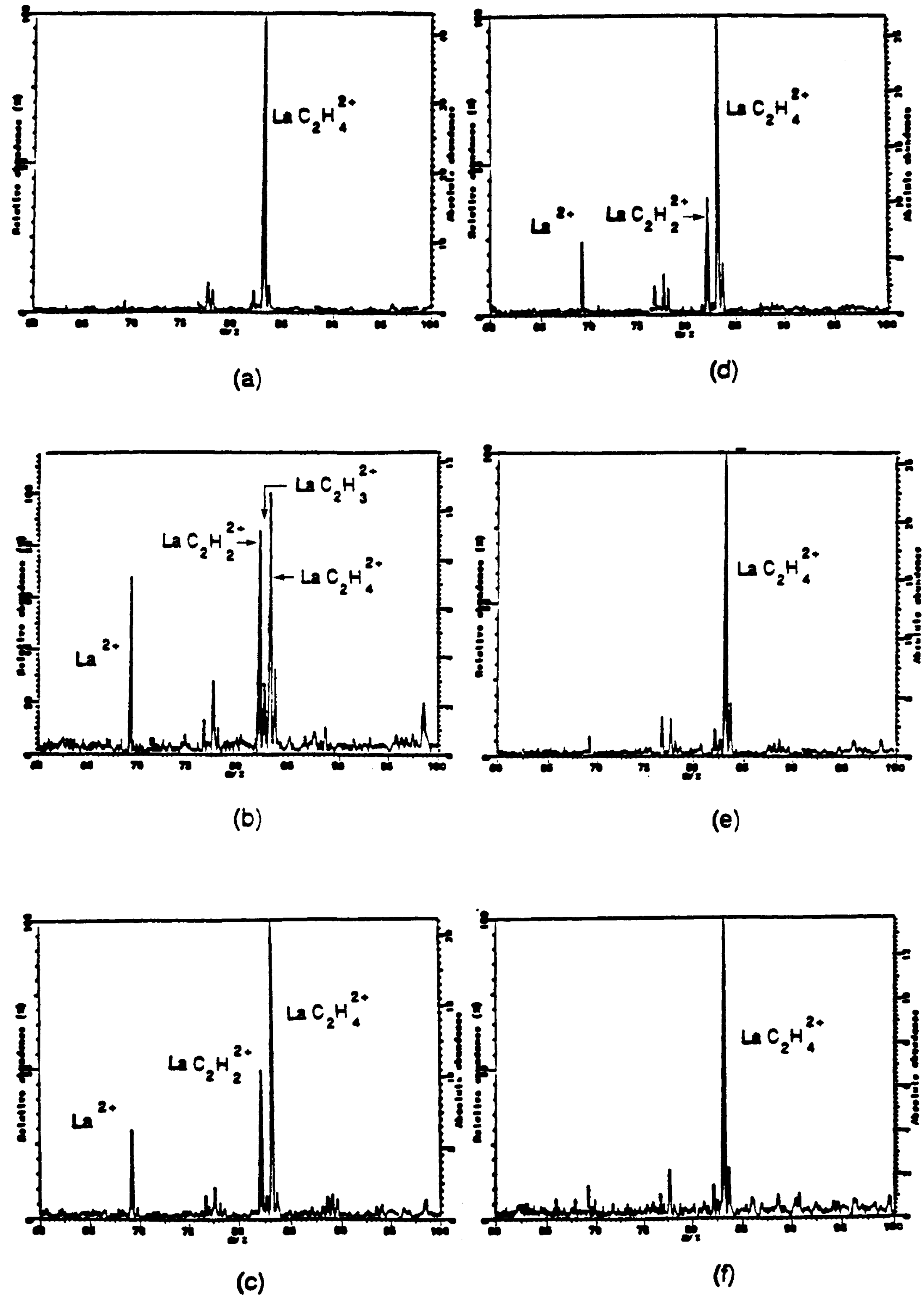


Figure 2. Photodissociation of LaC$_2$H$_4^{2+}$ ion with (a) no light present and white light with cutoff filters at (b) 437, (c) 568, (d) 602, (e) 703, and (f) 746 nm.

Table V. Product Ratios of the Reactions of La^{2+} with *n*-Butane and *n*-Butane-*1,1,1,4,4,4*-d_6

ion	neutral lost	%	ion	neutral lost	%
$LaC_4H_8^{2+}$	H_2	38	$LaC_4H_2D_6^{2+}$	H_2	33
			$LaC_4H_3D_5^{2+}$	HD	8
$LaC_4H_6^{2+}$	$2H_2$	11	$LaC_4H_4D_4^{2+}$ or $LaC_4D_6^{2+}$	D_2 $2H_2$	2
			$LaC_4H_2D_4^{2+}$	2HD (or $H_2 + D_2$)	3
			$LaC_4HD_5^{2+}$	HD + H_2	4
$LaC_3H_6^{2+}$	CH_4	6	$LaC_3H_3D_3^{2+}$	CHD_3	5
$LaC_2H_4^{2+}$	C_2H_6	34	$LaC_2H_2D_2^{2+}$	$C_2H_2D_4$	31
$LaCH_3^+ + C_3H_7^+$		8	$LaCD_3^+ + C_3H_4D_3^+$		9
$LaH^+ + C_4H_9^+$		3	$LaH^+ + C_4H_3D_6^+$		5

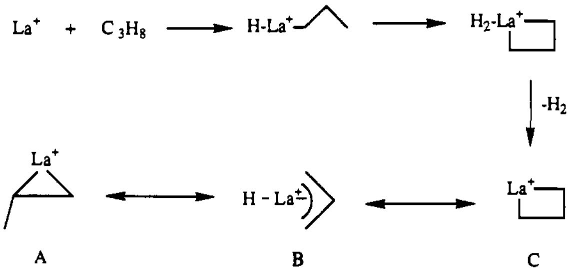
photodissociation of $LaC_3H_6^+$ or in most singly-charged organometallic ions. The energies required for the loss of H and H_2 can be determined directly and are equal to their thresholds yielding $D^\circ(LaC_3H_5^{2+}\text{–}H) = 43 \pm 5$ kcal/mol and $D^\circ(LaC_3H_4^{2+}\text{–}H_2) = 42 \pm 5$ kcal/mol. Again, the thresholds for reactions 25–28 may reflect sequential processes. As stated above, however, because the power density of the arc lamp at these longer wavelengths is low, it is likely that the thresholds for reactions 25–28 also give thermodynamic bond energies. Thus, reaction 27 gives $D^\circ(La^{2+}\text{–}C_2H_2) = 34 \pm 7$ (obtained using $D^\circ(La^{2+}\text{–}C_3H_6) = 42 \pm 5$ from reaction 28) which is somewhat lower, but within the range of $D^\circ(La^{2+}\text{–}C_2H_2) = 42 \pm 7$ kcal/mol obtained from reaction 15. Unfortunately, direct photodissociation of $LaC_2H_2^{2+}$ was not possible due to insufficient parent ion intensity.

A comparison of the bond energies of La^+ and La^{2+} indicates that for these limited cases the singly-charged species is bound as strongly or even more strongly than the doubly-charged species. This was certainly contrary to what one might expect based solely on electrostatic considerations and, thus, these results were brought to the attention of Bauschlicher and co-workers who performed detailed theoretical calculations on the same systems.[20] In Table III, the bond energies obtained by photodissociation (PDS), displacement reactions, and theory are compared, from which a "best estimate" of the bond energies is assigned. With the exception of $D^\circ(La^+\text{–}C_2H_2)$, the values are in excellent qualitative and quantitative agreement.

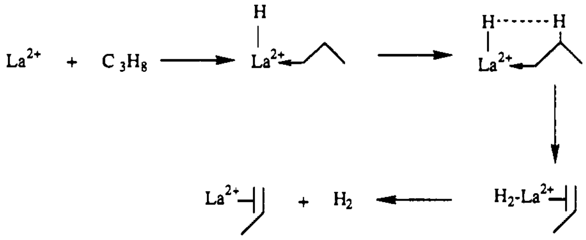
Reaction Mechanisms. Sc^+ was the first group 3 metal ion for which gas-phase ion–molecule reactions with alkanes were studied.[23] Compared to the more highly studied metals Fe^+, Co^+, and Ni^+ in groups 8–10, some unique chemistry was observed due to Sc^+ having two valence electrons. The chemistry of La^+ is similar to that of Sc^+.[13,21] La^+ (ground state $4s^25d^2$:^3F)[24] inserts into a C–H bond of C_3H_8 to undergo oxidative addition and subsequent reductive elimination of H_2, probably by a 1,3 process,[13] as shown in Scheme I. The most stable structure predicted from theoretical calculations is hydrido allyl structure B. Other possible structures, such as the metal inserted into the propene double bond A and the four-membered-ring structure C, are found to be 5 kcal/mol less stable.[20] Interestingly, CID on $LaC_3H_6^+$ yields a variety of products,[13] but no $LaC_3H_5^+$ or LaH^+ is observed. This suggests, but not unequivocally, that hydrido allyl structure B is not the most stable structure.

La^{2+} (ground state $4s^25d$:^2D)[24] has only one valence electron and, therefore, cannot undergo initial bond insertion to form two covalent bonds, like that in Scheme I. Instead, La^{2+} may proceed by the mechanism shown in Scheme II where, following hydrogen abstraction to form a LaH^{2+} center, the C_3H_7 radical uses its lone electron to form a weak dative bond with the metal or simply an ion induced-dipole complex, permitting the metal center to then abstract another H and form molecular hydrogen which is then eliminated. The final La^{2+}–propene complex is only electrostatically bound.[20] An alternative mechanism for dehydrogenation and alkane loss is presented in Scheme III. Because of the presence of the transition-metal ion species, symmetry restrictions of the intermediate that would otherwise occur may break down. Theoretical studies are currently underway to try to determine the mechanism.[25]

Scheme I



Scheme II



Looking once again at the photofragments from $LaC_3H_6^{2+}$, it is now possible to explain the loss of H and CH_3. Loss of these radicals from the C_3H_6 ligand will leave a radical behind which can form a strong σ bond with the lone electron on the La^{2+}. It is also interesting to compare the photodissociation fragmentation of $LaC_3H_6^{2+}$ to the fragmentation produced by collision-induced dissociation (CID). CID of $LaC_3H_6^{2+}$ produces La^{2+}, exclusively, at all of the energies studied. This is in direct contrast to $LaC_3H_6^+$ where, with increasing collision energy, CID is observed to give all of the products obtained from photodissociation reactions 17–21, and more.[13] Likewise, a comparison of $LaC_2H_4^{2+}$ and $LaC_2H_4^+$ leads to similar conclusions.[13] Another interesting observation is that, in analogy to $LaC_2H_4^{2+}$ discussed above, there are no singly-charged species seen in the photodissociation of $LaC_3H_6^{2+}$. The calculated curve crossing distance for La^+ and $C_3H_6^+$ of 11 Å (Table II) is apparently sufficiently long to prevent this pathway from competing effectively.

Finally, La^{2+} was reacted with *n*-butane-*1,1,1,4,4,4*-d_6 to further probe the reaction mechanism (Table V). Loss of H_2 and formation of LaH^+ show a remarkable selectivity for the methylene hydrogens, while loss of CHD_3 and formation of $LaCD_3^+$ incorporate the intact methyl group. These results together with the C_2H_6 elimination pathway are in accordance with Scheme III for butane, but they do not unequivocally prove its validity. In particular a mechanism along the lines of that shown in Scheme II for propane cannot be ruled out.

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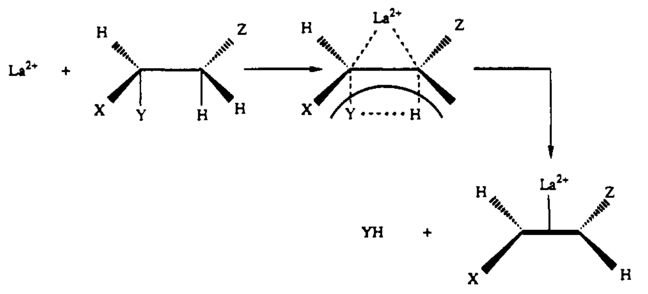
Scheme III



	Propane	Butane
X = CH_3 and Y = H loss of H_2	Z = H	Z = CH_3
X = H and Y = CH_3 loss of CH_4	Z = H	Z = CH_3
X = H and Y = C_2H_5 loss of C_2H_6		Z = H

Conclusions

This study adds to the increasing amount of evidence[14] that for group 3 metal ions, the extra valence electron of the singly-charged metal ion can result in stronger bonds being formed to unsaturated hydrocarbons than for the doubly-charged species, which bind electrostatically to these ligands. Theoretical studies confirm these results and provide additional details as to the exact nature of the bonding.[20,26] Currently, the only other system that we are aware of for which there are both experimental and theoretical studies is $NbCH_2^{n+}$ (n = 1 and 2). Interestingly in this case $D°(Nb^{2+}-CH_2) > D°(Nb^{+}-CH_2)$.[27]

While La^{2+} forms primarily electrostatic bonds to hydrocarbons, its single valence electron results in the formation of strong σ bonds to radicals. This characteristic is manifested in the photodissociation of $LaC_nH_{2n}^{2+}$ (n = 2, 3) species where, in contrast to $LaC_nH_{2n}^{+}$, loss of H and CH_3 were observed, yielding strong σ-bonded complexes with the remaining ligand.

The chemistries of La^+ and La^{2+} with simple alkanes are similar, with elimination of H_2 and small alkanes observed for both, although different mechanisms are clearly involved. One exception is the loss of alkene observed only for La^+, which is a consequence of its two-valence electronic structure as first observed for Sc^+.[23] One additional result from this study is that the second ionization potential of LaC_2H_2 is about 11 eV (Table IV). Surprisingly, it is close to that of lanthanum (11.06 eV), which is in contrast to the case of $NbCH_2^{2+}$ where it was found that upon the addition of the carbene, the second ionization potential was lowered from 14.3 to 12 ± 1 eV.[16] The combination of experiment and theory will continue to shed light on these interesting systems.

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Registry No. La^{2+}, 17643-88-8; $LaC_2H_4^+$, 128058-65-1; $LaC_2H_4^{2+}$, 128026-71-1; $LaC_3H_6^+$, 128026-67-5; $LaC_3H_6^{2+}$, 128026-73-3; $LaC_2H_2^+$, 128086-44-2; $LaC_2H_2^{2+}$, 128026-72-2; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8.

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Atmospheric Chemistry of Titan: Ab Initio Study of the Reaction between Nitrogen Atoms and Methyl Radicals

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Abstract: Ab initio calculations were performed on the reaction N + $CH_3 \rightarrow$ products. Optimized geometries have been calculated for all reactants, transition states, and products at the MP2/6-31G** level. Barriers and heats of reaction have been estimated by fourth-order Møller–Plesset perturbation theory with spin projection (PMP4(SDTQ)). Harmonic vibrational frequencies and zero-point energy corrections were calculated at the MP2/6-31G** level. The two-step process $N(^4S) + CH_3 \rightarrow {}^3[CH_3N] \rightarrow H_2CN + H$ appears to be the most important channel in this reaction.

Introduction

For the past 20 years, considerable research has been devoted to the atmospheres of Jupiter and its satellite Titan.[1] Early ground-based observations[1] indicate a large $[CH_4]/[H_2]$ ratio, which suggests that complex organic molecules could be formed via photochemical reactions. More recently, the Voyager missions have provided evidence that N_2 is the principal constituent of Titan's atmosphere,[1] followed by CH_4, H_2, C_2H_2, C_2H_4, C_2H_6, CH_3C_2H, C_3H_8, C_4H_2, HCN, HC_3N, C_2N_2, CH_2O, CO, CO_2, and H_2O. Consequently, in order to understand the dynamics of Titan's atmosphere, it is necessary to include reactions between nitrogen-containing species and hydrocarbons. The interaction of nitrogen atoms and methyl radicals is thought to be a significant path in the formation of HCN. Experimental rate constants obtained at room temperature by Stief et al.[2] and by Armstrong

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