

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/223130991>

Gas-phase hydrogen abstraction from methane using metal oxides. Theoretical study

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · APRIL 1991

Impact Factor: 2.78

CITATIONS

25

READS

3

2 AUTHORS, INCLUDING:



Lars G M Pettersson

Stockholm University

319 PUBLICATIONS 11,139 CITATIONS

SEE PROFILE

$$dP/dt = -N_T k_d P \quad (8)$$

in which k_d is the reaction rate and $N_T P$ is the triplet population. For the intensities involved in the experiment considered in Figure 7, N_T depends only weakly on intensity. Thus, this mechanism predicts an increase in hole depth with decreasing intensity at constant energy.

Comparison of the alternative single-color, one- or two-photon photochemical mechanisms is made in Figure 7. Clearly, only the triplet-triplet absorption mechanism is in agreement with the data. A $S_n \leftarrow S_1$ decomposition mechanism could show an intensity dependence qualitatively similar to that of the triplet-triplet absorption mechanism, but this mechanism may be rejected on

the basis of other experiments, as discussed above.

Acknowledgment. This research was supported by the Research Corp. with matching funds from the University of California, Riverside, and from the U.C.R. Committee on Research. M.A.I. acknowledges stipend support of NASA Training Grant NGT-50156. We thank Dr. Andre Yavrouian of the Jet Propulsion Laboratory for the purified PMMA and some samples of AT in PMMA. We also thank Mr. Kim Tran for obtaining the fluorescence lifetimes reported here.

Registry No. PMMA, 9011-14-7; AT, 28716-70-3; BrAT, 132751-53-2.

Gas-Phase Hydrogen Abstraction from Methane Using Metal Oxides. Theoretical Study

Knut J. Børve[†] and Lars G. M. Pettersson*

*Institute of Theoretical Physics, University of Stockholm, Vanadisvägen 9, S-113 46 Stockholm, Sweden
(Received: August 30, 1990)*

The abstraction of a hydrogen atom from methane using gas-phase LiO, MgO, and AlO has been studied at the SCF, CASSCF, and multireference CI levels. All reactions are exothermic by 6–14 kcal/mol but with high barriers of 6–16 kcal/mol. This is in accord with the negligible reaction rate observed experimentally at 296 K for AlO + CH₄. Computed spectroscopic parameters for AlOH are also given.

Introduction

The abstraction of hydrogen from methane as an initial step on the way to the formation of higher hydrocarbons presently attracts considerable attention. The reaction is catalyzed in the solid state by certain metal oxides such as La₂O₃ and Sm₂O₃.¹ Doping with lithium greatly enhances the reactivity of Sm₂O₃ and also changes MgO from being essentially inert into a relatively efficient catalyst. The reaction has been proposed² to be mediated by O[•] centers occurring in the oxide. These may be found near intrinsic cation vacancies or at other low-coordinated sites, such as steps or defects in the oxide crystal. They may also be generated by doping the crystal with alkali-metal ions. In this respect a highly increased activity toward formation of C–C bonds is found for Li/MgO, Na/CaO, and Li/Sm₂O₃.¹

Methyl radicals have been observed over MgO³ indicating the occurrence of hydrogen abstraction, while the kinetics of the methane consumption in the presence of O₂ indicate hydrogen abstraction from methane as the rate-limiting step.⁴ The reactive site is strongly indicated to be O[•] ions present at the surface. Indeed, O[•] centers on Mo/SiO₂ catalysts have been demonstrated to react with CH₄ also at low temperatures.⁵ Theoretical support for this has also been given by Anderson and co-workers,⁶ who performed calculations on cluster models of the MoO₃ oxide structure. They found O[•] to strongly activate C–H bonds and estimated the activation energy to be 16 kcal/mol.

We are currently performing a theoretical study of the hydrogen abstraction reaction over solid MgO and MgO doped with lithium or aluminum, and as an initial approach we have investigated the gas-phase reactions between the diatomic oxides (MgO, LiO, and AlO) and CH₄. These systems in themselves are of experimental interest, and very recently Parnis et al.⁷ reported on an experimental study of the gas-phase reactions of ground-state AlO with a number of different small molecules. Both association and abstraction reactions were studied, but although a number of complexes were formed in the former case, there was no indication

of any abstractions occurring. Thus, the barriers to abstraction were concluded to be substantial or larger than 5 kcal/mol.

In the gas phase MgO and LiO are expected to have very similar charge distribution, with oxygen having a charge of close to one electron. Assuming O[•] to be the active species, they should thus exhibit similar reactivities toward CH₄. In AlO, on the other hand, oxygen changes charge state close to the equilibrium bond distance,⁸ going from O[•] to O²⁻, which might affect its reactivity. The theoretical calculations have all been performed at high levels of approximation, using fairly large basis sets and accounting for both near-degeneracy effects and dynamical correlation. Since computed binding energies of the AlO and AlOH molecules have not been reported in the literature so far, we also present our best computed values for these systems.

Computational Details

The calculations have been performed at the SCF, CASSCF, and externally contracted multireference CI (CCI)⁹ levels of approximation. The reaction has been assumed to proceed collinearly with the C–H bond to be broken aligned with the M–O bond in the metal oxide (Figure 1). For the asymptotic limits the geometries of the respective systems were taken from experiment while the transition-state structures have been optimized at the CASSCF level by using pointwise calculations. The barrier

(1) Hutchings, G. J.; Woodhouse, J. R.; Scurrall, M. S. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 2507.

(2) Lin, C.-H.; Ito, T.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4808.

(3) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 58.

(4) Amorebieta, V. T.; Colussi, A. J. *J. Phys. Chem.* **1988**, *92*, 4576.

(5) Kaliaguine, S. L.; Shelimov, B. N.; Kazansky, V. B. *J. Catal.* **1978**, *55*, 384.

(6) Mehandru, S. P.; Anderson, A. B.; Brazdil, J. F.; Grasselli, R. K. *J. Phys. Chem.* **1987**, *91*, 2930.

(7) Parnis, J. M.; Mitchell, S. A.; Kanigan, T. S.; Hackett, P. A. *J. Phys. Chem.* **1989**, *93*, 8045.

(8) Lengsfeld III, B. H.; Liu, B. *J. Chem. Phys.* **1982**, *77*, 6083.

(9) Siegbahn, P. E. M. *Int. J. Quantum Chem.* **1983**, *23*, 1869.

[†] Current address: Institute of Chemistry, University of Bergen, Alle'gt 41, N-5007 Bergen, Norway.

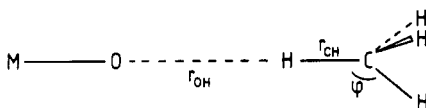


Figure 1. Collinear geometry for $\text{MO} + \text{HCH}_3$ abstraction reaction. Parameters r_{CH} , ϕ , and r_{OH} were optimized for the transition-state structure.

heights were then determined at the CCI level by using the computed CASSCF geometries. The Davidson correction (+Q)¹⁰ for higher excitations has been included in all reported CCI energies.

In the present section we will discuss the basis set selection, choice of active spaces for the CASSCF calculations, correlation level in the CI step, and strategy to find the transition-state structures. The calculations have to be balanced such that all the components in the two asymptotes, $\text{MO} + \text{CH}_4$ and $\text{MOH} + \cdot\text{CH}_3$, are equally well described. Thus, in particular, the hydrogen affinity of the metal oxide (MO) and the CH bond strength in CH_4 as well as the electron affinities of O and OH have to be described to a similar accuracy. Furthermore, for future use in studies of the reactions at a solid-gas interface, a reasonably economical description has to be developed.

The carbon basis set was the MIDI-4 [3s2p] basis¹¹ while the basis set for hydrogen was the Huzinaga (5s) basis¹² contracted to [3s] and extended with one p-function (0.8). Oxygen was described by use of the Dunning [4s3p] contraction¹³ extended with an even-tempered diffuse p-function and a d-function (1.0). The lithium basis set was the MIDI-3 basis of Tatewaki and Huzinaga¹¹ extended with three p-functions (1.5, 0.6, and 0.24). For magnesium and aluminum the MIDI-4 basis¹⁴ was used in most calculations with additional diffuse p-functions added (Mg: 0.2, 0.05; Al: 0.12) and in the case of Al also a d-function (0.18). In addition, substantially larger basis sets were used in calculations on the reactions with Al and Mg, using for O an (11s7p2d)/[5s4p2d] and for Al a (12s9p2d)/[6s5p2d] basis set following ref 8. The large basis set for Mg was (14s8p1d)/[10s6p1d] as given in ref 15.

In all the CASSCF calculations the bonds to be formed or broken were correlated, i.e., the C-H and the O-H bonds. In addition, the strongly occupied metal valence orbitals and electrons were included in the active space. Thus, $\text{Li}(2s^1)$, $\text{Mg}(3s^2)$, and $\text{Al}(3p^1)$ were always included in the active space, while the effect of including the $\text{Al}(3s^2)$ -derived molecular orbital in the CASSCF calculations was separately investigated. It was found that there is a large CAS effect from double excitations from 3s into 3p-derived π orbitals in AlOH and for the transition state. However, the resulting CAS space contains 14 000 configurations in C_s symmetry, and it was deemed impractically large in a multidimensional optimization process. Accordingly, the transition state was optimized with $\text{Al}(3s)$ inactive, and the energy of the so found transition state was then reevaluated with $\text{Al}(3s)$ active. The $\text{Al}(3s)$ -derived orbital was also active in the calculations on products and reactants. However, in AlO the main $\text{Al}(3s)$ correlation is obtained from $\sigma\text{-}\sigma^*$ excitations and a somewhat smaller active space is adequate. Finally, correlation of the oxygen (O^\cdot) π -like lone pairs was included to improve the electron affinity on oxygen in MO and MOH . The resulting active spaces in C_s symmetry were then (5,2)/7 for Li, (6,2)/8 for Mg, and (7,2)/9 or (8,3)/9 for Al where the number of active orbitals per symmetry (A', A'') and the number of active electrons are given. The active space was (5,2)/7 for transition-state optimization for the aluminum reaction.

TABLE I: Results for $\text{OH}(^2\Pi)$ and $\text{O}(^3P)$ Electron Affinities (EA in eV); Standard [4s4p1d] Basis Set Used on Oxygen

method	EA(OH)	EA(O)	ΔEA
SCF	-0.15	-0.58	0.43
CASSCF ^a	0.91	0.54	0.37
MR-CCI	1.35	0.93	0.42
MR-CCI+Q ^b	1.36	0.94	0.42
expt	1.83	1.46	0.37

^a CASSCF active space (2p,3p) orbitals. ^b Davidson correction included.

In the CCI based on the CASSCF calculations all configurations from the CASSCF wave function with a coefficient larger than 0.05 were taken as reference. In the correlated treatment the $\text{O}(2s)$ lone pair was included as well as all electrons from the CASSCF active space.

The M-O bond in the metal oxide and in the metal hydroxide have rather similar bond lengths. This is especially striking for magnesium where in MgO r_e is 1.75 Å while that of MgOH is 1.76 Å. In the case of LiO the reacting $^2\Sigma^+$ state has a bond distance very similar to r_e of LiOH , whereas the bond is 0.1 Å longer in the $^2\Pi$ ground state of LiO . For aluminum there is a decrease in bond length of 0.07 Å when going from AlOH to AlO . This is probably due to an element of π bonding that is found only in the oxide.

In the optimizations of the transition-state structures the metal-oxygen distance was thus always maintained at that of the ground state of the metal oxide. For magnesium and aluminum all energetics are also calculated with the metal-oxygen bond fixed at this value. The main effect of this simplification is an underestimate of the exothermicity of the reactions, and this is found to be less than 0.3 kcal/mol for magnesium and less than 1.7 kcal/mol for aluminum. For the lithium system all energetics are calculated with optimized Li-O distances since in this case there is a rather large gain in energy from relaxing the bond length when going from the $^2\Pi$ state of LiO .

Since the C-H bond distances in CH_4 and in the CH_3 radical are very similar, these were also kept fixed. The remaining geometry parameters to optimize for the transition state become the O-H and H-C distances and the umbrella angle of the H-CH_3 moiety. The structures were optimized in a two-step procedure with first a two-dimensional grid optimization of O-H and H-C for fixed angle, followed by an optimization of the angle at the optimized geometry. The distances were then reoptimized for the optimal angle. The transition-state structures were optimized by using the standard basis sets. In the case of Mg and Al the barriers were evaluated at optimized geometries by using the large basis sets.

In order to reliably predict the energetics of the abstraction reaction, the electron affinities of O and OH and the OH and CH bond strengths both have to be equally well described. The experimental electron affinities (EA) of $\text{O}(^3P)$ and $\text{OH}(^2\Pi)$ are 1.46¹⁶ and 1.83 eV,¹⁷ respectively. Computing the electron affinities by using ab initio techniques becomes extremely difficult due to the large differential effects of correlation and the diffuseness of the anion. At the SCF level both O and OH have negative electron affinities; i.e., the additional electron is not bound. However, as seen from Table I, the correlation contributions and basis set requirements are very similar for both systems such that the difference in EA is nearly independent of the method of calculation and is very close to the value obtained from experiment already at low levels of theory. Thus, the difference in EA is reliably described by using the present techniques for O and OH.

The overall abstraction reaction conserves the number of bonds in the system, with one C-H bond in CH_4 replaced by the O-H bond in MOH . If one uses the present basis sets for methane, the computed C-H bond strength (D_e) at the single-reference CCI+Q level with eight electrons correlated is 4.65 eV to be

(10) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974; Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Chem. Phys.* **1982**, *78*, 5682.

(11) Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205.

(12) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(13) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(14) Sakai, Y.; Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1981**, *2*, 100.

(15) Åkeby, H.; Pettersson, L. G. M. *Chem. Phys. Lett.* **1988**, *146*, 511.

(16) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1975**, *4*, 539.

(17) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740.

compared with the experimental value of 4.87 eV.¹⁸ A similar error, 0.27 eV, is made also in computing the O–H bond energy. In the actual calculations on the abstraction reaction we have only correlated the C–H bond that is actually dissociating. Since there is some coupling between the correlation effects, the result for the C–H binding energy is lower by 3 kcal/mol compared to when all bonds are correlated. However, this mainly affects the computed value for the exothermicities while the effect on the transition state is negligible.

Results and Discussion

In all cases the oxygen in the metal oxide is found with a charge of close to one extra electron. For LiO this results in a purely ionic interaction, while for MgO and AlO both covalent and polarization contributions to the bonding are found. This then results in somewhat different requirements on basis sets and wave function expansions in the different cases. The overall energetics of the reactions are very similar, however, with a large exothermicity of the order of 6–14 kcal/mol for all systems. This is combined with rather high barriers at 6–16 kcal/mol in the entrance channel of the reaction, in agreement with the recent experimental work of Parnis et al.⁷ where neither the abstraction reaction nor association of AlO with methane was observed at 296 K.

The lowest state of LiO is the $X^2\Pi$ state with a $\sigma^2\pi^3$ valence shell occupation. This state does not interact with collinearly approaching H–CH₃ since the H–C σ orbital is noninteracting by symmetry with the open π -shell of LiO. However, the $A^2\Sigma^+$ state with a $\sigma^1\pi^4$ occupation is, using the present basis sets, only 6.4 kcal/mol higher in energy; this state easily forms a three-center O–H–C bond to the approaching H–CH₃. In the C_s symmetry of the assumed reaction path the original σ and in-plane π orbitals of LiO are of the same symmetry and may easily mix to form the required bond to hydrogen for arbitrary Li–O–H angles. The collinear approach (180°) is energetically slightly preferred, however. The approach at 90°, which would be expected to be the most favorable for the initial interaction with ground-state LiO, would result in a 90° bent LiOH product which is some 10 kcal/mol higher in energy than the linear LiOH. To investigate which approach is preferred, we have located the transition state at 90° and 120° in addition to the collinear approach at 180° and have computed the energies at the obtained transition-state structure for angles in between. The collinear approach was found to result in the lowest transition-state energy, but the sensitivity to the angle is small; the transition state at 90° is only 1 kcal/mol higher in energy than that of the collinear approach. Thus, the required σ to π excitation of 6.4 kcal/mol of the LiO molecule for the collinear approach and the unfavorable (by 10 kcal/mol) 90° bent LiOH product for the 90° approach result in transition states of very similar energy. For the remaining discussion we will focus on the collinear approach from the excited $^2\Sigma^+$ state. The energetics for this reaction will be referred both to the $^2\Pi$ ground state and to the $^2\Sigma^+$ excited state.

Both MgO($X^1\Sigma^+$) and AlO($X^2\Sigma^+$) may form the required σ bond to H collinearly from their ground-state structures, and this is also the most favorable path for these reactions. For these systems one could also imagine the abstraction reaction to take place at the metal end. However, the linear AlOH is 2.0 and 3.6 eV lower in energy than the linear and 90° bent H–AlO, respectively. In all three conformers the charge on the oxygen is close to –0.8, while that of Al varies more strongly. In AlOH both Al and H transfer charge to the oxygen with the occupancy on Al close to $s^2p^{0.5}$, while with hydrogen attached to the Al end, all charge transfer to oxygen occurs from the Al. The Al becomes closer to sp^2 hybridized in this case, and only in the case of the linear HAlO conformer can this be compensated by additional π -type bonding.

The spectroscopic properties and electronic structure of AlO have been reported by Lengsfeld and Liu;⁸ however, they did not

TABLE II: Computed (CCI+Q) Spectroscopic Constants, Dipole Moment (μ_e in D), and Dipole Derivative (D/Å) for AlOH

$D_e = 5.56 \text{ eV}^a$	$\mu_e = 0.75 \text{ D}$
$r_e = 1.69 \text{ Å}$	$(d\mu/dr)_e = -6.6 \text{ D/Å}$
$\omega_e = 847 \text{ cm}^{-1}$	

^aDissociation to ionic products and corrected with experimental ionization potential of Al²² and electron affinity of OH.

TABLE III: Results for the Abstraction Reaction, MO + HCH₃ → MOH + ·CH₃ (All Energies in kcal/mol and Distances in Å)

	Exothermicity (–ΔE)			
	SCF	CASSCF	CCI+Q	expt
LiO($^2\Pi$)	5.4	24.1	17.2 (14.2) ^a	12.7
LiO($^2\Sigma^+$)	13.1	31.6	23.8 (20.8)	19.5
MgO($^1\Sigma^+$)	66.4	25.1	14.8 (11.8)	
MgO big basis	61.4	20.6	11.0 (8.0)	7.1
AlO($^2\Sigma^+$)	26.3	19.0	12.7 (9.7)	
AlO big basis	26.9	17.5	8.6 (5.6)	4 ± 5
	Barrier Height (E*) ^b			
	SCF	CASSCF	CCI+Q	
LiO($^2\Pi$)	39.4	16.0	13.0	
LiO($^2\Sigma^+$)	21.7	8.5	6.4	
MgO($^1\Sigma^+$)	12.5	9.7	9.2	
MgO big basis	15.7	13.1	10.9	
AlO($^2\Sigma^+$)	18.6	17.9	12.8	
AlO big basis	17.5	22.8	16.2	
	$E_{TS} - E_{prod}$			
	SCF	CASSCF	CCI+Q	
LiO	34.8	40.0	30.2	
MgO($^1\Sigma^+$)	78.9	34.9	24.0	
MgO big basis	77.1	33.8	21.9	
AlO($^2\Sigma^+$)	44.9	36.8	25.5	
AlO big basis	44.4	40.4	24.8	
	Transition-State Geometries			
	R_{OH}	R_{CH}	$\angle H-C-H$	$\angle M-O-H$
LiO	1.35	1.21	106.8	180°
	1.23	1.31	106.8	90° ^d
MgO	1.31	1.22	107	
AlO	1.33	1.21	107	

^aValues in parentheses corrected for effect of correlating remaining C–H bonds (see text). ^bBarrier computed for the entrance channel. ^cLi–O distance 1.59 Å ($A^2\Sigma^+$). ^dLi–O distance 1.69 Å ($X^2\Pi$).

report CI binding energies. Our larger basis set for AlO is identical with their GTO basis, and in our best calculations we obtain a binding energy D_0 of 4.85 eV, where the dissociation has been made to Al⁺ and O[–] and corrected to the neutral asymptote by using the experimental IP of Al and EA of oxygen. This should be compared with the experimental value of 5.26 eV.¹⁹ We feel it unlikely that, at this level of calculation, the theoretical value should be in error by as much as 0.4 eV and suggest that the experimental value might be somewhat high. For AlOH we have not been able to find earlier high-level theoretical results for the spectroscopic properties and thus report our computed MR-CCI+Q values in Table II. The optimization has been performed with a fixed O–H bond distance.

The exothermicities of the different reactions, excluding zero-point vibrations, may be obtained from

$$\Delta E = D_e(M-OH) + D_e(O-H) - D_e(H-CH_3) - D_e(M-O)$$

where M is Li, Mg, or Al and dissociation to ground-state components is assumed. Inserting the experimental values of 4.62 eV for $D_e(O-H)$ ²⁰ and 4.87 eV for $D_e(H-CH_3)$,¹⁸ the remaining quantity is the differential stability between the metal oxide and hydroxide. Using the values recommended by Bauschlicher et

(19) JANAF Thermochemical Tables, 3rd ed.; Dow Chemical: Midland, MI; *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. No. 1).

(20) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(18) Duchovic, R. J.; Hase, W. L.; Schegel, H. B.; Frisch, M. J.; Raghuvaran, K. *Chem. Phys. Lett.* **1982**, *89*, 120.

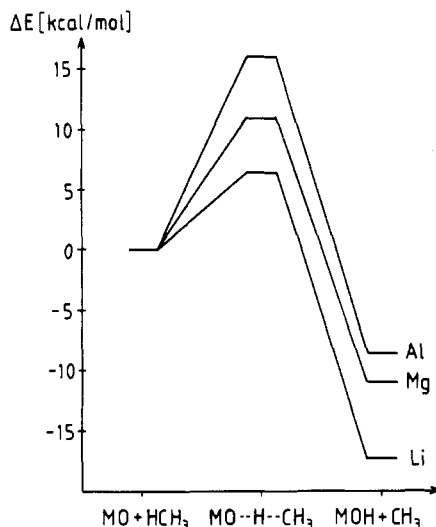


Figure 2. Comparison of the energetics (kcal/mol) of the abstraction reactions using $\text{LiO}(^2\Sigma^+)$, MgO , and AlO .

al.²¹ for Li and Mg, we obtain 0.80 and 0.56 eV, respectively, for this difference. The experimental exothermicities then become 12.7 and 7.1 kcal/mol for the reactions with LiO and MgO, respectively. For the reacting $^2\Sigma$ state of LiO the corresponding exothermicity becomes 20 kcal/mol. Using for $D_e(\text{AlO}-\text{H})$ 116 ± 5 kcal/mol (from ref 19 and assuming only O-H stretch) and for $D_e(\text{OH})$ 4.62 eV, we arrive at an estimated experimental exothermicity of 4 kcal/mol for the reaction with AlO.

Computing the exothermicities using the standard basis sets described above, we then find 17.2, 14.8, and 12.7 kcal/mol (see Table III) as our standard basis set values (CCI+Q) for the ground-state reactions of LiO, MgO, and AlO, respectively. The agreement with the experimental exothermicities at this level is within 9 kcal/mol, thus rather poor. In our calculations only one C-H bond has been correlated, leading to an underestimate of the C-H bond strength and thus to an overestimate of the computed exothermicity. Correlating also the remaining bonds in methane leads to a lowering of all computed exothermicities by 3 kcal/mol, which still in the case of the second-row metals are in error by 5 kcal/mol. The computed exothermicity for the Li reaction however has less than half the error. Improving the basis sets for Mg, Al, and O to the larger bases described results in decreased exothermicities and increased barrier heights, implying that the extended basis is more important for an adequate description of the oxide. These improved calculations result in exothermicities in close agreement with experiment; after correction for the remaining C-H correlation the discrepancy with the estimated experimental values is reduced to less than 2 kcal/mol.

It is interesting to note the large effects of near-degeneracy already on the computed exothermicities. In particular, the large decrease by more than 40 kcal/mol which is found in going from a single-configuration to a multiconfigurational wave function for MgO is noteworthy. At the SCF level the ionicity of the MgO molecule is strongly exaggerated, and a $\sigma^2 \rightarrow \sigma^{*2}$ excitation is required to improve the description of the covalent contribution to the bonding. The SCF level dipole moment is 8.8 D, while the CASSCF gives 5.9 D, in good agreement with the experimental value of 6.2 (6) D.²² Introducing correlation at the multireference

CCI level leads to a further improvement of the dipole moment to 6.1 D. This is consistent with a decrease in the total charge on oxygen from the SCF (-1.1) to the correlated levels (-0.8). For all the systems inclusion of correlation through the CCI results in a decrease in the computed CASSCF exothermicities by 7–10 kcal/mol, indicating that dynamical correlation is more important for the metal oxide than for the hydroxide.

The abstraction reaction proceeds by the formation of a three-center, two-electron σ bond between the oxygen, hydrogen, and carbon centers. This transforms into the O-H bond in the product hydroxide. Simultaneously, the radical character of LiO (initially on the oxygen) shifts over toward the methyl group. In AlO, the radical character is initially mainly concentrated on Al and becomes shared between the oxygen and carbon at the transition state. In MgO, finally, the MgO σ and σ^* orbitals interact with the carbon to generate the singly occupied orbitals on Mg in MgOH and of the methyl group. This is accompanied by polarization of the metal valence electrons and the metal-oxygen bond in the case of Mg and Al.

The optimized transition-state structures for the collinear approach are very similar for the three different oxides studied (Table III). The O-H bond distance varies only between 1.31 and 1.35 Å, and the C-H distance is between 1.21 and 1.22 Å in all cases. This can be compared with the equilibrium distance of 1.086 Å in CH_4 . The umbrella angle remains very close to tetrahedral while the CH_3 internal angle increases to close to 112° , approaching the 120° of the planar CH_3 radical. For LiO at angles different from collinear the transition state occurs somewhat later in the reaction, i.e., at shorter O-H distance and longer H-C distance. This is due to the less favorable final geometries in these cases.

The computed barriers correlate very nicely with the electronic structure of the oxides (Figure 2). $\text{LiO}(^2\Sigma^+)$ has an open σ orbital which interacts readily with the C-H σ bond, resulting in the lowest barrier. The higher barrier in the reaction with MgO results from the required transfer of charge from the oxygen to a polarized $\sigma(3s)$ orbital on the Mg. The highest barrier is obtained for AlO where the strength of the Al-O polarized π bonds is strongly reduced as a result of the movement of charge from Al(3p) to Al(3s). The opposite trends are found for the exothermicities. The computed barrier of 16 kcal/mol for the abstraction reaction with AlO provides strong support for the experimentally inferred high barrier for this reaction, based on the absence of an observed reaction in the experiment of Parnis et al.⁷ Increasing the Al and O basis sets increases the barrier height. Thus, the substantial barrier to hydrogen abstraction with gas-phase AlO is quite reliably confirmed.

Conclusions

The computed barriers to gas-phase hydrogen abstraction are found between 6 and 16 kcal/mol for the metal oxides (LiO, MgO, and AlO) studied in the present work. The lowest barrier obtained is found for the reaction with LiO, while AlO has the largest barrier at 16 kcal/mol, thus confirming the suggestion of Parnis et al.⁷ of a larger than 5 kcal/mol barrier to hydrogen abstraction for the $\text{AlO} + \text{CH}_4$ system.

Acknowledgment. Financial support from the Norwegian Research Council for Science and the Humanities is gratefully acknowledged for K.J.B.

Registry No. CH_4 , 74-82-8; LiO, 12142-77-7; MgO, 1309-48-4; AlO, 14457-64-8; AlOH, 20768-67-6.

(21) Langhoff, S. R.; Bauschlicher, C. W.; Partridge, H. In *Comparison of ab initio Quantum Chemistry with Experiment*; Bartlett, R., Ed.; Reidel: Boston, 1985.

(22) Büsener, H.; Heinrich, F.; Hes, A. *Chem. Phys.* **1987**, *112*, 139.

(23) Moore, C. E. Atomic Energy Levels. *Natl. Bur. Stand. (U.S.) Circ.* **1949**, No. 467.