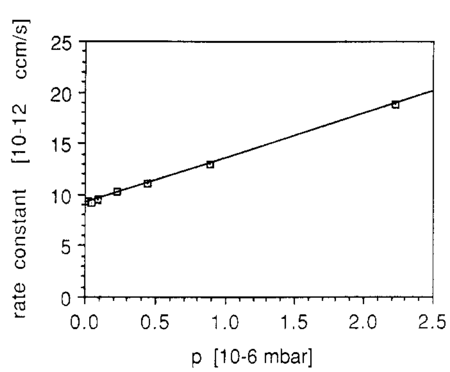

Figure 3. Variation of the apparent bimolecular rate constant, k_7, as a function of acetone pressure.

10^{-7} mbar an increase in disappearance rate with increasing pressure is evident.

The rate constants obtained by least-squares fit to the data of Figure 2 are plotted as a function of pressure in Figure 3, from which the numerical equation (14) may be obtained:

$$k_7 = 9.2 \times 10^{-12} + (1.8 \times 10^{-22})[\mathrm{M}] \quad (\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) \tag{14}$$

where [M] is the number density of acetone molecules in molecules $\mathrm{cm^{-3}}$. These data thus lead to values of k_b of 2.4×10^4 $\mathrm{s^{-1}}$ and k_r of 0.98×10^2 $\mathrm{s^{-1}}$. These values correspond to a unimolecular decomposition lifetime of 43 μs and a radiative emission lifetime of 10 ms. The production of the proton-bound dimer by radiative association is therefore more than 250 times slower than unimolecular decomposition of the chemically activated dimer, consistent with the failure to observe the proton-bound dimer at low pressure except under conditions of extremely long trapping time. The third-order rate constant for production of m/z 117 via collisional stabilization of 1.8×10^{-22} $\mathrm{cm^6\ molecule^{-2}\ s^{-1}}$ is extremely large, which is a result of the relatively slow unimolecular decomposition of the chemically activated species. For example, McEwan et al.[12] have measured the same quantity for proton-bound dimer formation in dimethyl ether to find a three-body rate constant 1.00×10^{-23} $\mathrm{cm^6\ s^{-1}}$. It is known from clustering studies of the energetics of proton-bound dimers of oxygen bases[19] that the interaction of $\mathrm{MH^+}$ with M is relatively constant in energy at 31 ± 1 kcal $\mathrm{mol^{-1}}$. Thus the extent of chemical activation in these complex proton-bound dimers is always the same. However, the number of normal modes of the complex ion may be varied considerably. The k_b for $[(\mathrm{CH_3})_2\mathrm{O}]_2\mathrm{H^+}$ of 7.69×10^4 $\mathrm{s^{-1}}$ obtained by McEwan et al.[12] is greater than the value of 2.4×10^4 $\mathrm{s^{-1}}$ obtained here for the acetone system. Thus these two systems give the expected effect of increased unimolecular dissociation rate with decreased number of normal modes of the complex. No comparable data were available for k_r for the other systems. We are currently in the process of exploring proton-bound-dimer formation in a variety of oxygen bases to more systematically probe the unimolecular decomposition and radiative processes and to model them using statistical theories of unimolecular reactions. The nature of the activated and emitting vibrational modes is an extremely complex question which may be able to be addressed by study of vibrationally dissimilar systems.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada, Bruker-Spectrospin (Canada), Spectrospin AG (Switzerland), and the Ontario Universities Research Incentive Fund is gratefully acknowledged.

---

(19) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6255.

Isotopic Evidence for Direct Methyl Coupling and Ethane to Ethylene Conversion during Partial Oxidation of Methane over Li/MgO

Peter F. Nelson,* Christopher A. Lukey,

CSIRO Division of Coal Technology, P.O. Box 136, North Ryde, New South Wales 2113, Australia

and Noel W. Cant

School of Chemistry, Macquarie University, New South Wales 2109, Australia *(Received: July 14, 1988)*

The products of the reaction of a $\mathrm{CH_4/CD_4/O_2}$ mixture over a Li-promoted MgO (Li/MgO) catalyst at 750 °C have been determined by mass spectrometry and high-resolution Fourier transform infrared spectroscopy. Under these conditions there was no significant hydrogen exchange between $\mathrm{CH_4}$ and $\mathrm{CD_4}$. $\mathrm{C_2H_6}$, $\mathrm{CD_3CH_3}$, and $\mathrm{C_2D_6}$ were the only ethanes detected, and $\mathrm{C_2H_4}$, $\mathrm{CD_2CH_2}$, and $\mathrm{C_2D_4}$ were the only ethylenes. The relative concentrations of the hydrocarbon products could be predicted on the basis of the relative concentrations of $\mathrm{CH_3}$ and $\mathrm{CD_3}$ determined by the kinetic isotope effect. The results suggest that the reaction proceeds almost exclusively by gas-phase methyl coupling and that ethylene is produced by gas-phase conversion of ethane.

Introduction

The partial oxidation of methane to form $\mathrm{C_2}$ and higher hydrocarbons is an alternative to conversion of methane into synthesis gas (by steam reforming or partial oxidation) and subsequent reaction of the synthesis gas to produce refinery or petrochemical feedstocks. Recently, a number of catalytic systems that result in methane conversions and $\mathrm{C_2}$ hydrocarbon selectivities of practical significance were reported.[1-7]

The mechanism for this reaction is believed to involve initially the homolytic cleavage of a C–H bond, resulting in the formation of $\mathrm{CH_3}$ radicals which undergo coupling to form $\mathrm{C_2H_6}$. The observation of a kinetic isotope effect ($k_\mathrm{H}/k_\mathrm{D}$) of 1.5 over a

---

(1) Keller, G. E.; Bhasin, M. M. *J. Catal.* **1982**, *73*, 9.

(2) Hinsen, W.; Bytyn, W.; Baerns, M. *Proc. Int. Congr. Catal., 8th* **1984**, *3*, 581.

(3) (a) Ito, T.; Lunsford, J. H. *Nature (London)* **1985**, *314*, 721. (b) Ito, T.; Wang, J.-X.; Lin, C.-H.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 5062.

(4) Otsuka, K.; Jinno, K.; Morikawa, A. *J. Catal.* **1986**, *100*, 353.

(5) Kimble, J. B.; Kolts, J. H. *Energy Prog.* **1986**, *6*, 226.

(6) (a) Sofranko, J. A.; Leonard, J. J.; Jones, C. A. *J. Catal.* **1987**, *103*, 302. (b) Jones, C. A.; Leonard, J. J.; Sofranko, J. A. *J. Catal.* **1987**, *103*, 311.

(7) Thomas, J. M.; Kuan, X.; Starchurski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 162.

0022-3654/88/2092-6176$01.50/0

Li/MgO catalyst at 750 °C[8] shows that C–H bond breaking is the rate-determining step in this reaction. However, the details of the methyl radical coupling mechanism have been debated. In a study of the catalytic oxidative coupling of CH_4 over metal oxides on an α-alumina support, Keller and Bhasin[1] proposed that the formation of C_2H_6 resulted from the surface coupling of adsorbed CH_3 radicals. On the other hand, Lunsford and co-workers[9] presented evidence for the existence of gas-phase CH_3 radicals during reactions over a Li-promoted MgO (Li/MgO) catalyst using a matrix isolation electron spin resonance (MIESR) technique. More recently,[10] using a modification of the MIESR apparatus, they showed that at least 45% of the C_2H_6 produced over Li/MgO could be accounted for by the gas-phase CH_3 radicals. Methyl radicals have also been detected by the Paneth lead mirror test over a Na-promoted Mn/SiO_2 catalyst operated with alternative methane and air feeds.[6b]

Another possible source of higher hydrocarbons in these catalyst systems is carbene, which was detected in the oxidative coupling reaction over Li/MgO by reaction with ethylene to yield cyclopropane.[11] It was not clear, however, whether the formation of cyclopropane was due to gas-phase CH_2 radicals or to carbene ligands on metal centers or whether the carbene participated directly in the oxidative coupling.

In this work we present isotopic evidence for direct methyl coupling and ethane to ethylene conversion during the partial oxidation of methane over Li/MgO. A feed gas consisting of an equimolar mixture of CH_4 and CD_4 was used, and the compositions of the methanes, ethanes, and ethylenes produced were determined by mass spectrometry (MS) and high-resolution Fourier transform infrared (FTIR) spectroscopy.

Experimental Section

The Li/MgO catalyst was prepared by slurrying Li_2CO_3 and MgO (Li:Mg = 0.12 atomic ratio) and heating the product to a thick paste which was air dried overnight at 170 °C. Analysis of the catalyst showed levels of other metals to be less than 350 ppm except for Sr (1230 ppm) and Al (1300 ppm). After calcination at 900 °C for 4 h in air the catalyst was crushed and the −1.2 + 0.6 mm fraction was separated for use. Ultrahigh-purity CH_4 (99.9% minimum), high-purity N_2 (99.99%), and industrial O_2 (99.5% minimum) were used without further purification. CD_4 was supplied by MSD Isotopes (99.4 atom % D).

The experiment was performed at atmospheric pressure using a flow system and a fixed bed tube reactor (recrystallized alumina, 99.7%) packed with 101 mg of Li/MgO. The catalyst was maintained at 750 °C, and the feed gas was 90% CH_4 (or an equimolar mixture of CH_4 and CD_4) and 10% O_2 at a total flow rate of 47 mL/min, corresponding to a pseudocontact time (W/F) of 0.034 (g s)/mL.

Feed and product gas analyses were made by gas chromatography (GC) using a Chromosorb 102 column coupled to thermal conductivity (TCD) and flame ionization detectors (FID) in series. Analyses of CH_4 and CD_4 at equal concentrations showed no significant differences in response to the FID, and identical responses were also assumed for C_2H_6 and deuteriated ethanes and C_2H_4 and deuteriated ethylenes. The effluent from the reactor was connected to the inlet system of a quadrupole mass spectrometer (VG SX-200) operated in the multiple-ion monitoring mode.

Samples of feed and product gas were also collected in an infrared gas cell (10-cm path length), and gas-phase FTIR spectra were obtained with a Digilab FTS 20/80 spectrometer. The spectra were recorded at 0.25-cm^{-1} resolution by the coaddition of 256 scans.

TABLE I: Methane Conversion, Oxygen Consumption, and Product Selectivities over Li/MgO Catalyst (T = 750 °C, W/F = 0.0342 (g s)/mL)

feed gas	CH_4	CH_4	50% CH_4/50% CD_4	CH_4
run time, min	15	36	69	194
CH_4 conversion, %	5.0	5.0	4.5	4.8
O_2 consumption, %	40	39	28	36
selectivities, %				
CO	6.9	7.2	8.4	9.5
CO_2	23.7	23.7	26.7	25.0
C_2H_4	16.5	16.0	13.9	14.5
C_2H_6	50.4	50.7	49.1	49.0
C_3H_6	0.9	0.8	0.7	0.7
C_3H_8	1.5	1.5	1.2	1.3

TABLE II: Composition of Methanes and Ethanes Determined by Quadrupole MS

species	m/e	rel concn[a]	species	m/e	rel concn[a]
CH_4	16	100	C_2H_6	30	100
CH_3D	17	3	C_2H_5D	31	<3
CH_2D_2	18	2	$C_2H_4D_2$	32	[b]
CHD_3	19	4	$C_2H_3D_3$	33	91
CD_4	20	100	$C_2H_2D_4$	34	4
			C_2HD_5	35	2
			C_2D_6	36	25

[a] The relative concentrations of CH_4 and C_2H_6 are equal to 100. [b] Not determined due to interference by O_2.

Results and Discussion

Results for methane conversion, oxygen consumption, and selectivities to hydrocarbon and carbon oxide products are given in Table I. The catalyst was initially exposed to 100% CH_4, then 50% CH_4/50% CD_4, and finally 100% CH_4 again. From the results for 100% CH_4 at 15, 36, and 194 min on stream there is a suggestion that some minor deactivation of the catalyst occurred in the course of the experiment with methane conversion decreasing from 5.0% to 4.8% and oxygen consumption decreasing from 40% to 36%. Methane conversion and oxygen consumption for 50% CH_4/50% CD_4 are, however, significantly lower and reflect the kinetic isotope effect previously observed for this catalyst.[8]

Product gas compositions for methanes and ethanes determined by MS are given in Table II. This composition was determined from the signals recorded for m/e 16–20 (methanes) and 30–36 (ethanes). These were corrected for contributions from the feed gas, for the natural abundances of ^{13}C, ^{17}O, ^{18}O, and, in the case of the ethanes, for fragmentation patterns and relative sensitivities obtained from the literature.[12] Some corrections were also made to the signal for m/e 30, to eliminate possible contributions from deuteriated ethylenes. Because of the large number of corrections, the results presented in Table II are subject to considerable uncertainty, particularly those for the C_2H_6, C_2H_5D, and $C_2H_2D_4$ ethanes. However, it is clear that there is very little exchange among the methanes, with CH_4 and CD_4 being the only species detected in significant concentrations. The results for the ethanes are complicated by the large contribution from O_2 to m/e 32. There is also some ambiguity about some of the assignments of compounds to particular m/e values (e.g., m/e 33 can be CH_2DCD_2H or CD_3CH_3). However, the only ethanes observed in significant concentrations correspond to C_2H_6, $C_2H_3D_3$, and C_2D_6. Thus, in spite of the associated uncertainties, these results suggest that exchange of H and D in this system is of minor importance, both for the reactant hydrocarbon, methane, and for the major hydrocarbon product, ethane.

Low concentrations of the deuteriated methanes CH_3D and CD_3H observed by FTIR confirmed that exchange of H and D between the methanes was insignificant. The analyses of product C_2 hydrocarbons were complicated by the large absorptions due to CH_4 and CD_4 and overlapping signals from product CO and CO_2. However, these contributions could be successfully subtracted to obtain spectra for the ethanes and ethylenes. The

---

(8) Cant, N. W.; Lukey, C. A.; Nelson, P. F.; Tyler, R. J. *J. Chem. Soc., Chem. Commun.* **1988**, 766.

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

(10) Campbell, K. D.; Morales, E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 7900.

(11) Martin, G.-A.; Mirodatos, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1393.

(12) Amenomiya, Y.; Pottie, R. F. *Can. J. Chem.* **1968**, *46*, 1735.

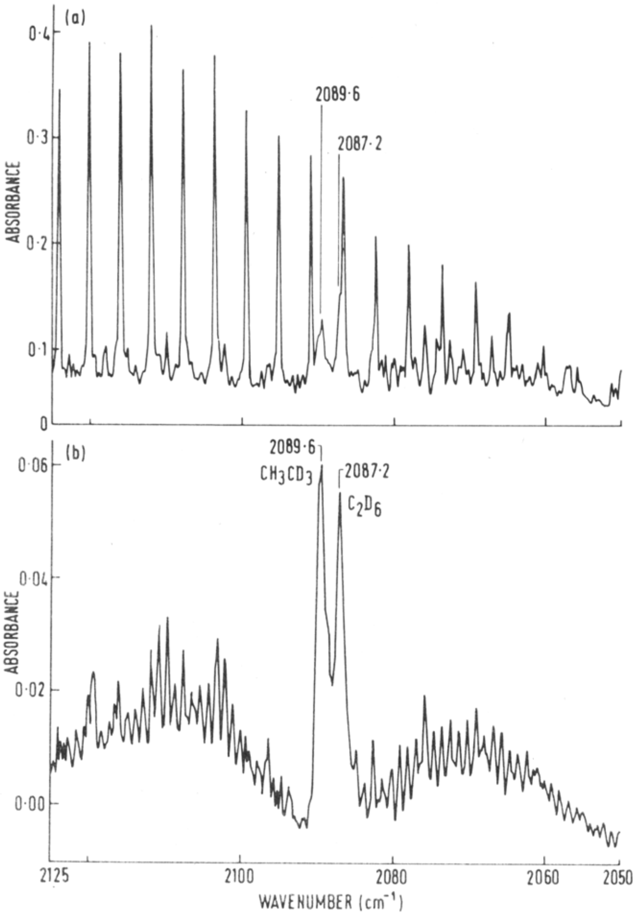

Figure 1. FTIR spectra: (a) product gas spectrum, 2125–2050 cm^{-1}; (b) difference spectrum of (a) minus CD_4 and CO.

subtractions were performed with spectra of feed gas (to remove CH_4 and CD_4 lines) and product gas from an experiment with CH_4 alone (to remove CO and CO_2 lines). These spectra were obtained under the same conditions as those for the CH_4/CD_4 product gas in order to minimize effects of pressure broadening on line shape.

Figure 1a shows the product gas spectrum in the 2125–2050-cm^{-1} region. The rotational lines of CO are evident, and there are also less intense lines due to CD_4. Figure 1b shows a difference spectrum with CO and CD_4 subtracted. The peaks at 2089.6 and 2087.2 cm^{-1} are assigned to CH_3CD_3 and C_2D_6, respectively. These assignments are based on literature values,[13-15] and that for C_2D_6 was confirmed by an experiment in which CD_4 alone was fed to the catalyst and the product gas spectrum obtained. These peaks are due to combination bands which have significant absorption due to Fermi resonance.

Similarly, Figure 2a shows the product gas spectrum in the 980–600-cm^{-1} region. The intense absorption from 980 to 900 cm^{-1} is due to CD_4 and that from 720 to 620 cm^{-1} to CO_2. The lines centered at 822.4 cm^{-1} may be assigned to the C–C bending mode of C_2H_6[13,14] and that at 751.2 cm^{-1} to the out-of-plane bend of CD_2CH_2.[13] Figure 2b shows the difference spectrum resulting from the subtraction of the CD_4 features from a CH_4/CD_4 feed gas spectrum. The lines at 949.8, 922.6, 915.8, and 909.1 cm^{-1} may be assigned to the out-of-plane bend of C_2H_4 on the basis of literature values[13] and the product gas spectrum obtained with CH_4 alone in the feed gas. The line at 943.5 cm^{-1} may be assigned to another out-of-plane bending mode of CH_2CD_2.[13]

Figure 2c presents the difference spectrum obtained by subtracting the product gas spectrum with CH_4 alone from the spectrum shown in Figure 2b to remove the CO_2 contribution between 720 and 620 cm^{-1}. Since more C_2H_4 and C_2H_6 were produced from the CH_4 feed gas, the peaks due to these species appear negative and confirm these assignments. The CO_2 subtraction reveals the absorption at 720.2 cm^{-1} (underlying a line due to CO_2) due to the out-of-plane bend of C_2D_4,[13] confirmed by feeding CD_4 alone. Thus, the only ethanes and ethylenes detected in the FTIR spectra were C_2H_6, CD_3CH_3, C_2D_6, C_2H_4, CD_2CH_2, and C_2D_4. No significant absorption was observed at frequencies quoted in the literature for other ethanes and ethylenes.

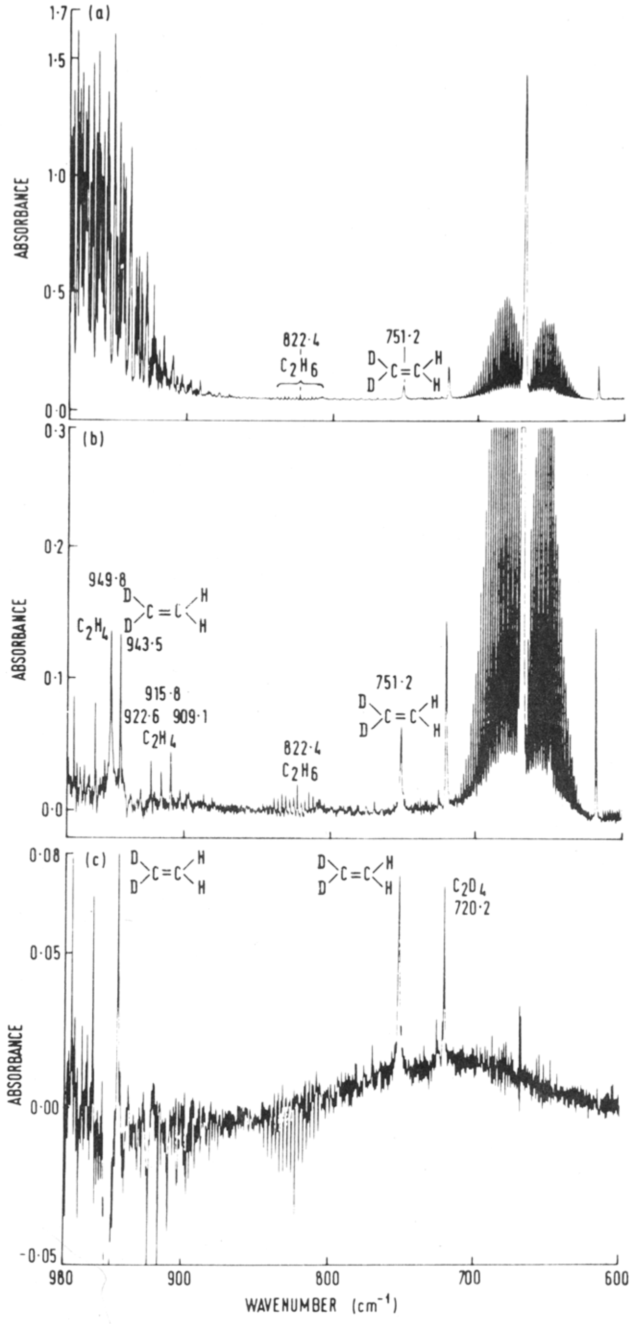

Figure 2. FTIR spectra: (a) product gas spectrum, 980–600 cm^{-1}; (b) difference spectrum of (a) minus CD_4; (c) difference spectrum of (b) minus CO_2.

The contributions of the detected species to the total ethane and ethylene concentrations were determined from the GC analyses and calibrations for the FTIR absorptions obtained for experiments with CH_4 or CD_4 alone as feed gas. Calibrations for C_2H_6, C_2D_6, C_2H_4, and C_2D_4 were possible using the lines at 822.4, 2087.2, 949.8, and 720.2 cm^{-1}, respectively. The absorptions for these species in the experiment with CH_4/CD_4 feed gas could then be used to determine the contributions to the total ethane and ethylene concentrations. Assuming that CD_3CH_3 is the only

---

(13) Pinchas, S.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic: New York, 1971.

(14) Van Riet, R. *Ann. Soc. Sci. Bruxelles, Ser. 1* **1957**, *71*, 102.

(15) Nakagawa, I.; Shimanouchi, T. *J. Mol. Spectrosc.* **1971**, *39*, 255.

J. Phys. Chem. **1988**, *92*, 6179–6182

TABLE III: Relative Concentrations of Ethanes and Ethylenes in CH_4/CD_4 Experiment (FTIR Measurements)

	calcd[a]	obsd		calcd[a]	obsd
C_2H_6	34 ± 2	36 ± 4	C_2H_4	34 ± 2	34 ± 2
CD_3CH_3	49 ± 2	(49)[b]	CD_2CH_2	49 ± 2	(51)[b]
C_2D_6	17 ± 2	15 ± 2	C_2D_4	17 ± 2	15 ± 2

[a] For k_H/k_D = 1.4 ± 0.1. [b] By difference.

other ethane and CD_2CH_2 is the only other ethylene, the contribution of these species may be determined by difference. Table III presents these results together with calculated values based on the kinetic isotope effect (k_H/k_D = 1.4 ± 0.1) and a statistical distribution since the mixed species are more likely than the symmetrical ones. The uncertainty in the magnitude of the kinetic isotope effect is due to the small difference in the results obtained with CH_4 alone. The experimental results are in excellent agreement with the calculations and show that exchange of H and D in the product hydrocarbons is insignificant and that the product distribution reflects the relative concentrations of CH_3 and CD_3.

The results may therefore be interpreted as confirmatory evidence for the coupling of methyl radicals in this catalytic system. However, the absence of any significant hydrogen exchange between CH_4 and CD_4 and also between the product C_2 hydrocarbons is surprising since MgO exhibits activity for CH_4/D_2 exchange at 300 °C[16] and activity for CH_4/CD_4 exchange at 400 °C.[17] It is therefore likely that the methyl coupling reaction occurs almost exclusively in the gas phase. This is in agreement with Lunsford's conclusion[10] that at least 40–45% of the C_2 products were accounted for by gas-phase methyl coupling. The results also suggest that ethane is the source of the ethylene since the distribution of the deuteriated ethylenes is not significantly different from that of the ethanes. It is possible that conversion of ethane to ethylene also occurs predominantly in the gas phase since the gas-phase abstraction reaction to form an ethyl radical and further reaction of the ethyl to produce ethylene will preserve the isotopic distribution, and this mechanism has been well-established for hydrocarbon combustion reactions.[18] However, the participation of the surface in the ethane-to-ethylene conversion cannot be discounted.

Data for methyl radical concentrations obtained by Lunsford and co-workers[9,10] and the overall rate constant[19,20] for the gas-phase exchange reactions

$$CH_4 + CD_3 \rightarrow CH_3 + CD_3H$$

$$CD_4 + CH_3 \rightarrow CD_3 + CH_3D$$

suggest that these reactions could make a significant contribution to the small amount of exchange observed in the methanes. However, in the absence of a direct measurement of the methyl concentration under the conditions of the present experiment, it is not possible to evaluate the contribution of these reactions exactly.

The results also show that the participation of carbene or methylene radicals in this system is probably not significant since the reactions postulated[11] to produce ethane

$$CH_2 + CH_4 \rightarrow CH_3 + CH_3$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$

would lead to exchange in the ethanes.

These observations obviously have considerable implications for the development of a practical methane conversion process, particularly for the optimization of ethylene yields.

Acknowledgment. This work was supported by a NERDDP grant to BHP, Melbourne Research Laboratories.

Registry No. CH_4, 74-82-8; MgO, 1309-48-4; Li, 7439-93-2; deuterium, 7782-39-0; methyl radical, 2229-07-4.

---

[16] Utiyama, M.; Hattari, H.; Tanabe, K. *J. Catal.* **1978**, *53*, 237.

[17] Quanzhi, L.; Amenomiya, Y. *Appl. Catal.* **1986**, *23*, 172.

[18] Warnatz, J. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1008.

[19] Burcat, A.; Lifshitz, A. *J. Chem. Phys.* **1970**, *52*, 3613.

[20] Chen, C.-J.; Back, M. H.; Back, R. A. *Can. J. Chem.* **1977**, *55*, 1624.

"Double-Rydberg" Molecular Anions

Maciej Gutowski,[†]

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Jack Simons,* Ramon Hernandez, and Hugh L. Taylor

Chemistry Department, University of Utah, Salt Lake City, Utah 84112 (Received: August 11, 1988)

We present results of ab initio electronic structure simulations which predict the electronic stability of molecular anions each consisting of a closed-shell cation core with two "Rydberg-like" outer electrons. Earlier experimental work by the Bowen group and theoretical calculations of Cardy et al. and of Ortiz on NH_4^- suggested that such species might exist. Our calculations on H_3^-, $H_3CH_2^-$, NH_4^-, H_3O^-, H_2F^-, and NeH^- indicate that, except for H_3^-, all of these species are electronically stable at geometries near those of the corresponding cation "cores". For all of these species, there also may exist long-lived metastable states whose decay to underlying neutral-molecule states requires the ejection of one electron and the "shake down" rearrangement of a second orbital. The symmetries, electronic energies, and local geometrical stabilities of the above species have been examined and are discussed here.

Introduction

In 1987, the Bowen group[1] at Johns Hopkins University reported observations which lead them to suggest that NH_4^- may exist as a stable or long-lived species in a tetrahedral structure resembling the NH_4^+ cation with two diffuse electrons "orbiting" the cation core. The weak electron binding energy (ca. 0.5 eV) combined with the sharp peak observed in the photoelectron spectrum supported their conjecture.[2] Ab initio calculations[3] by Cardy et al. and by Ortiz gave further support to this novel

---

[†] On leave at the Chemistry Department, University of Utah, Salt Lake City, UT 84112.

[1] In 1985, the Bowen group reported photoelectron data on NH_4^- in its normal form (e.g., as solvated H^-): Coe, J. V.; Snodgrass, J. T.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1985**, *83*, 3169. At the Fall, 1987 American Chemical Society meeting in New Orleans, Bowen reported on this same species and noted a weak peak corresponding to a NH_4^- species with an electron binding energy near 0.5 eV. Details of this report are available in the Ph.D. thesis of J. T. Snodgrass, The John Hopkins University, 1987, and in an article by K. H. Bowen and J. G. Eaton in Proceedings of the International Workshop on the Structure of Small Molecules and Ions (to be published).

0022-3654/88/2092-6179$01.50/0