radicals with small organic molecules.[24]

The dramatic difference between the measured A factors for the addition of CH_3S to 1,3-butadiene and allene is difficult to explain. Further work on the products of these two addition reactions may be required to satisfactorily explain the observed differences.

Conclusion

We have measured the kinetics of the reactions of CH_3S with a variety of unsaturated hydrocarbons. In all cases, we observe behavior that we attribute to an addition reaction leading to a CH_3S–alkene complex. In the case of 1,3-butadiene, this complex is in equilibrium with the reactants, and we are able to extract thermodynamic information from the measured equilibrium constants. At higher temperatures, there appears to be another channel in the reaction of CH_3S with allene which we attribute to hydrogen abstraction. Because of the slow rate of reaction with simple alkenes and apparent lack of reactivity with O_2,[9] it appears that the primary fate of CH_3S in the atmosphere is reaction with NO_x.

Oxidative Dimerization of Methane over Magnesium and Calcium Oxide Catalysts Promoted with Group IA Ions: The Role of $[M^+O^-]$ Centers

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Abstract: The oxidative dimerization of CH_4 to C_2H_4 and C_2H_6 over MgO and CaO is strongly influenced by certain group IA ions which are employed as promoters. Lithium is an effective promoter for MgO, but sodium and potassium are not; all three group IA ions are effective promoters for CaO. Centers of the type $[M^+O^-]$ (M^+ is a substitutional group IA ion) are present in each active and selective catalyst, which supports the hypothesis that these centers are active for the formation of $CH_3^•$ radicals and, therefore, in the overall oxidative dimerization reaction.

Lithium-promoted MgO is a reasonably active and selective catalyst for the oxidative dimerization of CH_4 to C_2H_6 and C_2H_4 (C_2 compounds).[2] Selectivities of 50% have been achieved at a CH_4 conversion level of 38%. The reaction is believed to occur via surface-generated methyl radicals which couple mainly in the gas phase. It has been proposed that the active sites for the formation of $CH_3^•$ radicals are $[Li^+O^-]$ centers[2,3] or surface O^- ions which are in equilibrium with these centers.[4] In this paper additional evidence is given for the role of these and analogous centers of the type $[M^+O^-]$ in the activation of CH_4. (Here M^+ is a substitutional group IA ion in a group IIA oxide.) The present study also provides a comparison of the activities and selectivities which may be achieved over MgO and CaO promoted with Li^+, Na^+, or K^+ ions.

The $[M^+O^-]$ centers have been extensively studied by Abraham and co-workers[5-8] in single crystals of the host oxide. The $[Li^+O^-]$ centers exist in equilibrium with molecular oxygen at elevated temperatures and may be trapped in MgO and CaO by quenching the sample.[6] More generally, $[M^+O^-]$ centers may be formed by irradiation of the doped group IIA oxides at low temperatures. Although most of the spectroscopic work has been carried out on single crystals, $[Li^+O^-]$ centers recently have been studied in polycrystalline Li/MgO catalysts.[4]

Experimental Section

All catalysts were prepared by evaporating to dryness a slurry which contained either MgO or CaO (Aldrich, 99.999%) and the appropriate group IA carbonate. The resulting materials contained ca. 30 atomic percent alkali-metal ion, which was present mainly as the carbonate. That is, only a small fraction of the group IA ions was incorporated into the host lattice, even after activation at elevated temperatures.

The catalytic experiments were carried out in a fixed-bed flow reactor. The catalysts were dehydroxylated under flowing O_2 and then maintained in the reactant gas mixture at 700 °C for 16 h before rate data were obtained. The EPR experiments were carried out on catalysts which had reached a steady state in the flow reactor and were subsequently heated in 170 Torr of O_2 at 650 °C for 1 h before quenching. After the EPR spectra on these samples were obtained, they were warmed to 25 °C under vacuum and then irradiated ($\lambda = 254$ nm) at 77 K under 120 Torr of O_2 for 1 h.

Results and Discussion

A comparison of activity and selectivity for different combinations of group IA/group IIA oxide catalysts is given in Table I. No attempt was made to maximize yield; thus the value of 12.8% obtained for the Li/MgO catalyst is considerably less than the value of 19.4% which was obtained previously under different conditions.[2]

It is most significant that among the MgO catalysts, only Li/MgO exhibited a moderate level of conversion and selectivity, and, therefore, a relatively good C_2 yield. Although Na/MgO was a poor catlayst at temperatures <700 °C, Na/CaO was a good catalyst, which rivaled Li/MgO in C_2 yield. This observation indicates that *specific* interactions, such as the formation of $[M^+O^-]$ centers, are important in the activation of methane, at least over the range of temperatures reported here.

Evidence for the $[M^+O^-]$ centers is indeed found in the EPR spectra (Figure 1) of Li/CaO and Na/CaO, both of which gave good C_2 yields. Conversely, no $[M^+O^-]$ signal was observed in the Na/MgO and K/MgO catalysts, which did not give good C_2 yields at temperatures <700 °C. The EPR spectra of the $[M^+O^-]$ centers are characterized by $g_\parallel = 2.000$–2.004 and $g_\perp = 2.054$–2.109, depending on the particular group IA ion and the host oxide.[5-8] The spectrum of the $[Li^+O^-]$ center in the used

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Table I. Comparison of MgO and CaO Catalysts Promoted with Group IA Ions

	MgO				CaO			
	pure	Li	Na	K	pure	Li	Na	K
wt %[a]	0	7	20	30	0	5	15	23
SA, $m^2\ g^{-1}$	12	4	6	7	6	2	2	2
convn,[b] % (CH_4)	10.2	22.6	11.9	11.5	23.4	10.8[c]	22.0	21.9
C_2 sel,[d] %	6.3 (0.3)[e]	56.7 (1.0)	17.8 (0.5)	0.7 (0.0)	8.1 (0.1)	67.2[c] (0.7)	51.1 (0.9)	41.5 (0.7)
C_2 yield, %	0.6	12.8	2.1	0.1	1.9	7.3	11.2	9.1
$[M^+O^-]$	no	yes	no	no	no	yes	yes	no[f]

[a] Atomic ratio of group IA/IIA ions = 0.43 (based on group IA carbonate–group IIA oxide). There was no significant loss of Li or Na during the period of reaction. [b] 1 g of MgO, 0.8 g of other catalysts; reaction run at 700 °C, 76 Torr of CH_4, 37 Torr of O_2, 647 Torr of He, 0.92 mL s^{-1}. [c] At 750 °C the conversion and selectivity were 22.9% and 52.8%, respectively. [d] Other major products were CO and CO_2; the CO_2:CO ratio was >10 for all catalysts except MgO and K/MgO. Small amounts (<1%) of CH_3OH, HCHO, C_3H_6, and C_3H_8 were observed. [e] Numbers in parentheses refer to ethylene:ethane ratios. [f] A small concentration of $[Na^+O^-]$ was observed, but no $[K^+O^-]$ was detected.

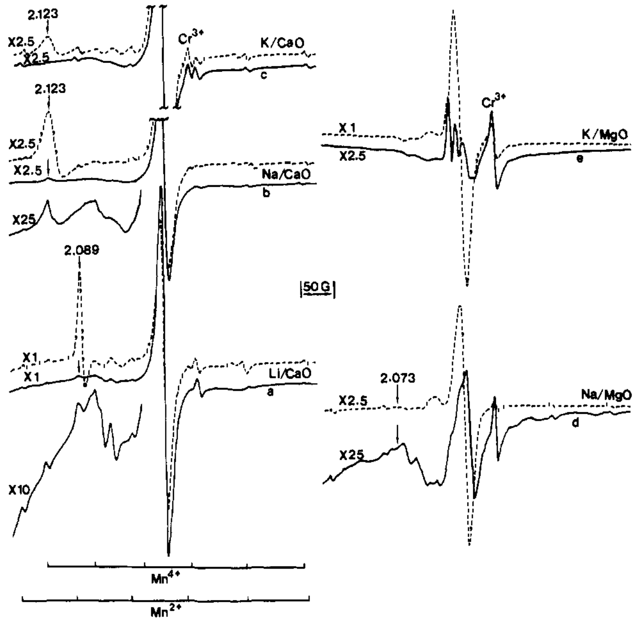

Figure 1. EPR spectra at 77 K of (a) Li/CaO, (b) Na/CaO, (c) K/CaO, (d) Na/MgO, and (e) K/MgO: (—) quenching, (---) after irradiation.

Li/MgO catalyst, formed both by quenching and by irradiation at 254 nm, has been reported previously.[2-4] The $g_\perp$ values of 2.089 and 2.123 for $[Li^+O^-]$ and $[Na^+O^-]$, respectively, in CaO are in excellent agreement with the results reported for single crystals.[7]

With the polycrystalline K/CaO catalyst the results are less definitive. No $[M^+O^-]$ centers were observed upon quenching, but irradiation yielded a small $g_\perp$ component at 2.123, which suggests the presence of $[Na^+O^-]$ centers. Analysis of the CaO indicated that 0.006 wt % Na was present as an impurity. No evidence for $[K^+O^-]$ centers with $g_\perp = 2.073$ was found in this sample following irradiation. As noted by Abraham et al.,[8] K^+ is expected to behave differently than Li^+ or Na^+ because of its larger ionic size, and, indeed, it is surprising that K^+ fits at all into the CaO lattice.[9] The C_2 yield reported in Table I may result from $[K^+O^-]$ centers which are formed at the CaO surface but which are too low in concentration to be detected by EPR, or it may result from an active potassium oxide phase (see below).

The effect of size mismatch is even more evident in the K/MgO samples.[9] Neither in the single crystals nor in the polycrystalline catalysts is there evidence for $[K^+O^-]$ centers in MgO. With Na/MgO one again has a borderline case with respect to ionic radii.[9] A $[Na^+O^-]$ signal having $g_\perp = 2.072$ was observed upon irradiation of single crystals,[7] but not upon quenching.[6] With the used catalyst no clear signal was evident at this g value after either treatment. It is significant to note that in the preparation of the single crystals the sodium ions were incorporated into the MgO during crystal growth in an arc furnace,[10] i.e., near the melting point of MgO. By contrast the catalyst samples used to obtain the data of Table I and the spectra of Figure 1 had never been heated above 700 °C; therefore the diffusion of Na^+ into MgO was minimal.

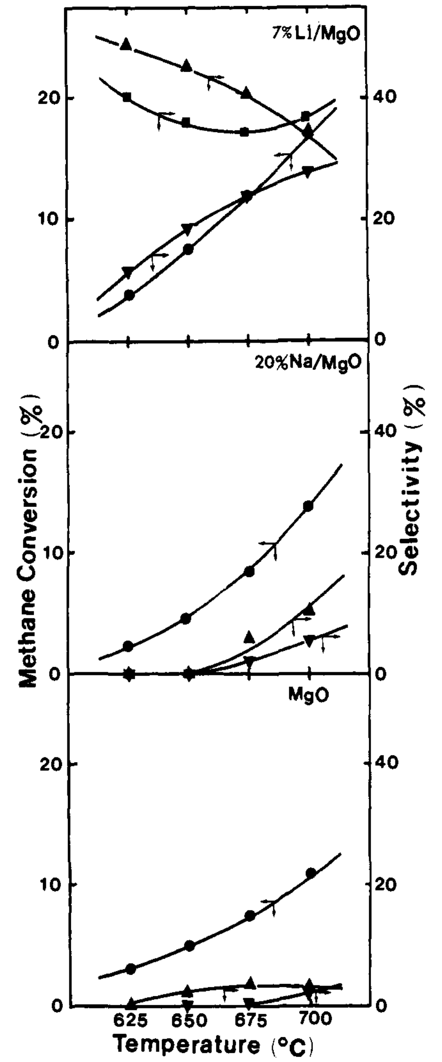

Figure 2. The effect of temperature on activities and selectivities over 1.0 g of 7% Li/MgO, 20% Na/MgO, and low surface area MgO: ●, CH_4 conversion; ▼, C_2H_4 selectivity; ▲, C_2H_6 selectivity; ■, C_1 selectivity. CH_4 (76 torr) and O_2 (38 torr) were used at a flow rate of 0.92 mL s^{-1}.

Aika and co-workers,[11] however, have reported recently that a Na/MgO catalyst, prepared by heating a sample to 800 °C, was active and selective for C_2 formation at 750 °C. In order

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[9] Ionic radii for the relevant ions are Li^+ (0.68 Å), Na^+ (0.97 Å), K^+ (1.33 Å), Mg^{2+} (0.66 Å), and Ca^{2+} (0.99 Å). Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*: 66th ed.; CRC: Boca Raton, FL, 1986; p F-164.

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to determine whether the more severe thermal treatment and catalytic reaction at 800 °C was responsible for the improved yield, we prepared used catalysts (20% Na/MgO) in this manner and then quenched them from 750 °C. Again, there was no spectral evidence for $[Na^+O^-]$ centers after quenching or after subsequent irradiation.

A comparison of the catalytic results for Li/MgO, Na/MgO and pure MgO, as depicted in Figure 2, indicates that among the three catalysts Na/MgO was unique in that C_2 selectivity began to develop only at temperatures greater than 675 °C and continued to increase at 700 °C. When the conversion and selectivity are extrapolated to 750 °C, the C_2 yield is about 15%, which is comparable to the value of 16% reported by Aika and co-workers.[11] Similarly a 20% Na/MgO catalyst prepared and operated under the same conditions as employed by the Japanese group gave a C_2 yield of 11% at 750 °C. Since no $[Na^+O^-]$ centers were detected in this material, it appears reasonable that another type of active site was formed, such as $Na^+O_2^-$ which resulted from the decomposition of the Na_2CO_3 phase at the higher temperatures. By contrast, the activity and selectivity patterns obtained for Na/CaO are more similar to Li/MgO (Figure 2) than to Na/MgO,[12] which supports the role of $[M^+O^-]$ centers in the former catalysts.

Thus, although $[M^+O^-]$ centers appear to be involved in the activation of CH_4 on catalysts where the cation size match is appropriate, other centers involving group IA ions may be active, particularly at temperatures >700 °C. Moreover, other catalysts such as La_2O_3 are effective in generating $CH_3^\bullet$ radicals, yet they do not contain group IA ions.[13,14] It should be noted, however, that thermally generated O_2^- ions have been detected on La_2O_3, and this may be the reactive form of oxygen on the lanthanide oxides.[15]

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Generation of the Distonic Ion $CH_2NH_3^{\bullet+}$: Nucleophilic Substitution of the Ketene Cation Radical by Ammonia and Unimolecular Decarbonylation of Ionized Acetamide[†]

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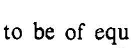
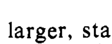
Abstract: The combined application of Fourier-transform ion cyclotron resonance and tandem mass spectrometries, complemented by ab initio MO calculations, provides a relatively detailed description of crucial aspects of the potential energy surface of ionized acetamide ($CH_3CONH_2^{\bullet+}$, **6**) and the complexes formed in ion/molecule reactions of ionized ketene ($CH_2CO^{\bullet+}$, **5**) with ammonia. Both the unimolecular decarbonylation of **6** and the bimolecular substitution of **5** generate the distonic ion $CH_2NH_3^{\bullet+}$, which is fully characterized by proton-transfer reactions and collision-induced dissociations. Although the two fundamentally different reactions are linked by common intermediates, which are suggested to be hydrogen-bridged complexes, there are some distinct differences. The reaction of ammonia with $CH_2CO^{\bullet+}$ to generate $CH_2NH_3^{\bullet+}$ and CO occurs in a region of the potential energy surface which does not result in the formation of hydrogen-scrambled product ions. In contrast, starting from $CH_3CONH_2^{\bullet+}$ the isomerization steps involve intermediates which, prior to the formation of $CH_2NH_3^{\bullet+}$ and CO, permit hydrogen-exchange processes to occur. The enol of ionized acetamide ($CH_2{=}C(OH)NH_2^{\bullet+}$, **8**) is separated by a significant barrier from $CH_3CONH_2^{\bullet+}$. If **8** is internally excited it also dissociates to $CH_2NH_3^{\bullet+}$ and CO, presumably via $CH_3CONH_2^{\bullet+}$. Recent suggestions that nucleophilic substitutions involving radical cations are "forbidden" processes and should therefore have an inherent, low reactivity are not confirmed. The substitution reaction $NH_3 + CH_2{=}C{=}O^{\bullet+} \rightarrow CO + CH_2NH_3^{\bullet+}$ is relatively facile.

Distonic ions[1] such as **1** are species where the charge and radical sites are, in a formal sense, centered at different atoms. Such radical ions have been known in mass spectrometry and radiation chemistry for quite some time.[1d] In the past, distonic ions were often proposed as high-energy, though stable, intermediates to account for specific unimolecular decompositions or rearrangements of radical cations, and only recently they were recognized as species in their own right.[1-3] In the last years these ions have regained experimental interest[1d,2] because calculations[3] predicted some of them to be of equal, if not larger, stability than the corresponding conventional isomers such as **2**.[4]



$\overset{\bullet}{C}H_2{-}\overset{+}{N}H_3$

1



$CH_3{-}\overset{+\bullet}{N}H_2$

2

[†] Dedicated to Professor Th. J. de Boer on the occasion of his retirement from the University of Amsterdam.

[‡] Berlin.

[⊥] Amsterdam.

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