for organic synthesis. Results of similar studies with aminocarbenes promise even wider application and will be reported in due time.

A typical experimental procedure follows.

Chromium-carbene complex **1** (0.30 g, 1.20 mmol) was placed in a 30-mL Pyrex test tube which was then sealed with a rubber septum and evacuated and purged with argon (3×). *N*-Vinylacetamide (0.12 g, 1.39 mmol) in 20 mL of degassed dry acetonitrile was added by syringe, and the resulting solution was irradiated for 15 h (450-W Conrad-Hanovia 7825 medium pressure mercury lamp, Pyrex well). The solvent was then removed under vacuum, and the yellow residue was dissolved in ethyl acetate, filtered through Celite, diluted with one volume of hexane, and permitted to air oxidize overnight in a light box (6-20 W Vitalite fluorescent bulbs). Filtration of the brown suspension, solvent removal, and evaporative distillation (0.2 mm, ~120 °C) gave 0.18 g (72%) of **2d** as a colorless viscous oil.

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Supplementary Material Available: Full characterization and spectral data (^{1}H NMR, ^{13}C NMR, and IR) for all new compounds (4 pages). Ordering information is given on any current masthead page.

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Catalytic Partial Oxidation of Methane over BaPbO$_3$: Possible Involvement of Peroxide Ion

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Although numerous metal oxides catalyze the oxidative dimerization of methane to higher hydrocarbons,[1] the nature of the catalytically active sites is substantially unknown. Previous speculation that peroxide or superoxide ions are responsible for methane activation over Sm$_2$O$_3$[2] and over Na$^+$/MgO at high temperatures[3] is supported by the fact that several simple peroxides, e.g., Na$_2$O$_2$, SrO$_2$, and BaO$_2$, can stoichiometrically oxidize methane.[4] Here we show, for the first time, the existence of peroxide ions on a complex metal oxide surface that catalyzes the oxidation of methane to C$_2$ hydrocarbons. We suggest that these peroxides may exist in a novel, through-bond isomer similar electronically to ozone.[5]

Table I. Steady-State Methane Oxidation over BaPbO$_3$[a]

space velocity (h^{-1})	P_{CH_4} (torr)	P_{CH_4}/P_{O_2}	C$_2$ productivity[b] [mmol·(g cat)$^{-1}$·h^{-1}]	C$_2$ selectivity[c] (%)	C$_2$ yield[d] (%)
13300	323	4.4	16.0	60.4	14.0
9100	100	2.4	6.0	51.8	18.0
10000	106	2.2	7.8	48.1	16.3
21100	100	2.5	9.4	68.8	13.7

[a] BaPbO$_3$ (0.35-0.55 g), 875 °C. [b] Defined as mol of CH$_4$ converted to C$_2$ products per g catalyst per h. [c] Typically, the C$_2$H$_4$/C$_2$H$_6$ ratio was 1.1. [d] The C$_3^+$ yield was <1%.

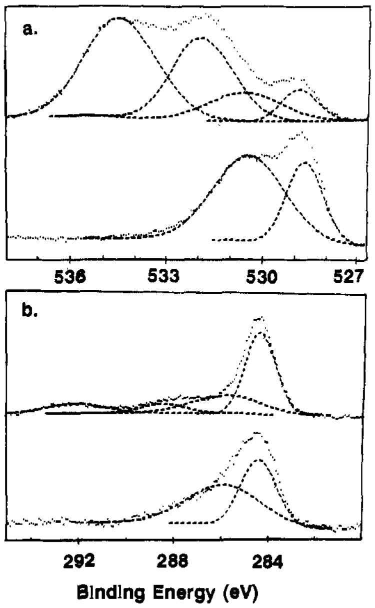

Figure 1. XPS spectra of unused (bottom) and used (top) BaPbO$_3$ catalysts. a. O$_{1s}$ region bottom: O^{2-}, 528.4 eV; O$_2^{2-}$, 530.1 eV; top: O^{2-}, 528.6 eV; O$_2^{2-}$, 530.3 eV; CO$_3^{2-}$, 531.6 eV; HCO$_3^-$, 534.1 eV. b. C$_{1s}$ region bottom: 284.6 eV (by definition) and 286.1, adventitious C; top: 284.6 eV (def.) and 286.1, adventitious C; CO$_3^{2-}$, 288.7 eV; HCO$_3^{2-}$, 292.3 eV.

Barium metaplumbate[6] was treated in flowing O$_2$ for several hours before beginning the oxidation reaction. As shown in Table I, moderate yields and high C$_2$ selectivities were obtained at 875 °C in a conventional 4 mm ID plug-flow reactor when the initial O$_2$ to CH$_4$ molar ratio was ~0.5. No methane oxidation was observed in similar experiments wherein quartz chips replaced the BaPbO$_3$ catalyst. These steady-state results were obtained after 2 h on stream; however, constant C$_2$ productivity was observed initially. This lack of an induction period for C$_2$ production is consistent with the hypothesis that the BaPbO$_3$ surface is responsible for the catalytic activity.

The XPS spectrum[7] of BaPbO$_3$ after annealing overnight in flowing O$_2$ at 875 °C, shown in the lowers traces of Figure 1, indicates that this material is not a typical A^{2+}B^{4+}[O^{2-}]$_3$ perovskite.[8] The binding energies and relative intensities (2.0:1.0)

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(7) X-ray photoelectron spectra were acquired with an H.P. 5950A spectrometer equipped with an Al Kα source, a quartz monochromator, and a flood gun that was set at 1.0 V, 0.3 mA. Analyzer chamber pressures were less than 5×10^{-9} Torr. Binding energies were determined with respect to adventitious carbon whose binding energy was defined as 284.6 eV.[17]

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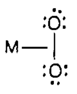
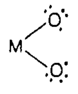
of the O_{1s} peaks at 530.1 and 528.4 eV are consistent with a formulation of $Ba^{2+}Pb^{2+}[O_2]^{2-}O^{2-}$. The O_{1s} binding energy for peroxide dianions in Na_2O_2 and BaO_2 are 530.4 and 530.9 eV, respectively; O^{2-} binding energies are about 528–529 eV.[9] The absence of a feature at about 289 eV rules out the presence of $CO_3{}^{2-}$ on the surface whose O_{1s} spectrum interferes with that of peroxide dianion.[10] The Pb $4f_{7/2}$ photoelectron peak was markedly asymmetric; qualitatively similar XPS peak shapes have been observed in both atomic and synthetic metals.[11] The surface composition is $Ba_{1.0}Pb_{1.7}[O_2{}^{2-}]_{2.0}O^{2-}{}_{2.1}$.

The photoelectron spectrum, shown in the upper traces of Figure 1, of a used catalyst after several hundred turnovers is more complex than that of the unused catalyst. New features at 534.1 and 292.5 eV in the O_{1s} and C_{1s} regions, respectively, are assigned to the $HCO_3{}^-$ ion since the O/C atomic intensity ratio is 3.1 and the binding energies for these two new peaks are similar to those observed in $NaHCO_3$.[9] A broad, unresolved signal extending from 285 to 289.5 eV appears different from the high binding energy shoulder of adventitious carbon in the O_2-annealed sample and probably includes some $CO_3{}^{2-}$. If the 531.3 eV O_{1s} peak were derived solely from carbonate, the corresponding C_{1s} carbonate peak would be both very broad (>3 eV) and centered at unreasonably low binding energies (<288.5 eV). Thus the 531.3 eV feature arises from both carbonate and the peroxide of $BaPbO_3$. Therefore the 528.2 O_{1s} peak and the Pb $4f_{7/2}$ peak at 137.4 eV (not shown) are assigned to $BaPbO_3$. The Ba $3d_{5/2}$ spectrum (not shown) may be deconvoluted into three Gaussian components that correspond to $BaPbO_3$, $Ba(HCO_3)_2$, and $BaCO_3$. The overall surface composition is $Ba_{3.9}Pb_{1.0}C_{2.7}O_{8.7}$. These results indicate that (1) $BaPbO_3$, hence the peroxide dianion, remains at the surface, (2) the surface becomes partially covered with $BaCO_3$ and $Ba(HCO_3)_2$, and (3) the surface becomes deficient in lead. Bulk analytical results show that about 20% of the lead is lost under relevant catalytic conditions.

The unusual nature of the peroxide ions in $BaPbO_3$ deserves comment. Relativistic stabilization of the Pb 6s band[12] may cause an oxidation of the O 2p band with the result that $BaPbO_3$ is better described as $Ba^{2+}Pb^{2+}[O_2]^{2-}O^{2-}$ rather than $Ba^{2+}Pb^{4+}[O^{2-}]_3$. Independent evidence,[13] consistent with this hypothesis, is provided by an analysis of the IR reflectance spectra of the $BaPb_{1-x}Bi_xO_3$ system which indicates unusually low effective charges on the oxygen atoms that vary from −1.18 for $x = 1$ to −0.6 for $x = 0.35$. The XPS and IR results[13] provide evidence concerning charge distribution, not local geometry. *Classical* inorganic peroxides exist as diatomic, through-space spin-coupled species **1a** with O–O distances of 1.45–1.50 Å.[14] Crystallographic analyses[15] of $BaPbO_3$, based on a profile refinement of powder data and which unfortunately includes high-R factors, indicates O···O contacts of ~3.0 Å. These results suggest that a *nonclassical* through-bond species **1b** may occur in $BaPbO_3$ and perhaps in other superconducting oxides[8,16] reported to exhibit similar XPS features attributed to peroxide anions, as well.



1a



1b

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE-8617436.

Registry No. $BaPbO_3$, 12047-25-5; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; Na_2O_2, 1313-60-6; BaO_2, 1304-29-6; O^{2-}, 16833-27-5.

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Potent Inhibition of 5-Enolpyruvylshikimate-3-phosphate Synthase by a Reaction Intermediate Analogue

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5-Enolpyruvylshikimate-3-phosphate synthase (EPSP synthase, E.C. 2.5.1.19) catalyzes the reversible transfer of the carboxyvinyl moiety of phosphoenolpyruvate (PEP) to the 5-hydroxyl group of shikimate 3-phosphate (S3P). From a commercial standpoint, it is the most important enzyme in the shikimic acid pathway since it is the target of the broad spectrum herbicide glyphosate (*N*-phosphonomethylgylcine).[1-3] A number of isotope labeling and kinetic studies[4,5] have supported the proposal of Levin and Sprinson[6] that the enzymatic reaction proceeds via an addition–elimination mechanism (Scheme I), and the isolation of tetrahedral adduct **1** by Anderson et al.[7] has provided the final proof. We now report the synthesis of the two diastereomers of phosphonate **2**, a stable analogue of intermediate **1**, and their evaluation as reaction intermediate analogue inhibitors of EPSP synthase.

Inhibitors **2r** and **2s** are synthesized from (−)-shikimic acid as shown in Scheme II. Rhodium diacetate-catalyzed coupling[8] of acetonide **3**[9] with methyl (dibenzylphosphono)diazoacetate **4**,[10] followed by alkylation of the potassium salt of the resulting ether **5**, affords compound **6** in 63% overall yield. Acid-catalyzed cleavage of the acetonide moiety, followed by cyclization to lactone **7**, takes place in 79% yield. The free hydroxyl group of **7** is

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