

# Chromium Dioxide Cation $\text{OCrO}^+$ in the Gas Phase: Structure, Electronic States, and the Reactivity with Hydrogen and Hydrocarbons<sup>1</sup>

Andreas Fiedler, Ilona Kretzschmar, Detlef Schröder,\* and Helmut Schwarz\*

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany

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**Abstract:** The potential-energy surface of the triatomic cation  $[\text{Cr}_2\text{O}_2]^+$  has been examined by means of ion-cyclotron resonance and sector-field mass spectrometry as well as high-level theoretical methods. Chromium(V) dioxide cation  $\text{OCrO}^+$  can be generated by electron ionization of  $\text{CrO}_2\text{Cl}_2$  and exhibits a doublet ground state. The experimentally determined  $\text{IE}(\text{CrO}_2)$  of  $9.7 \pm 0.2$  eV leads to  $\Delta H_f(\text{OCrO}^+) = 209 \pm 12$  kcal/mol which compares well with a theoretical prediction of 217 kcal/mol. The high-valent chromium(V) dioxide  $\text{OCrO}^+$  slowly reacts with  $\text{H}_2$  to form  $\text{CrO}^+$  and  $\text{H}_2\text{O}$  as products. Activation of saturated and unsaturated hydrocarbons, including methane and benzene, is much more efficient and involves C–H as well as C–C bond activation. In the reaction of  $\text{OCrO}^+$  with  $\text{CH}_4$  the by-product  $\text{OCr}(\text{OCH}_2)^+$  points to the operation of a stepwise mechanism in that initially a single oxo unit in  $\text{OCrO}^+$  is activated in terms of a [2 + 2] cycloaddition of methane across the Cr–O double bond. A structurally different  $[\text{Cr}_2\text{O}_2]^+$  cation can be generated by chemical ionization of a mixture of  $\text{Cr}(\text{CO})_6$  and  $\text{O}_2$ . The experimental findings together with the computations propose that the ions formed consist of a mixture of doublet and quartet states of the dioxide  $\text{OCrO}^+$  and the dioxygen complex  $\text{Cr}(\text{O}_2)^+$  ( ${}^6\text{A}''$ ); in the latter the dioxygen unit is end-on coordinated to the metal. Due to spin conservation, the direct formation of the doublet ground state  $\text{OCrO}^+$  ( ${}^2\text{A}_1$ ) from the ground state reactants  $\text{Cr}^+$  ( ${}^6\text{S}$ ) and  $\text{O}_2$  ( ${}^3\Sigma_g^-$ ) is not possible; rather, two curve crossings from the sextet via the quartet to the doublet surface in the sequence  ${}^6\text{Cr}^+ + {}^3\text{O}_2 \rightarrow {}^6\text{Cr}(\text{O}_2)^+ \rightarrow {}^4\text{OCrO}^+ \rightarrow {}^2\text{OCrO}^+$  are suggested.

## Introduction

Oxidation reactions with high-valent chromium compounds are widely applied in organic synthesis.<sup>2</sup> Besides classical reactions, such as the oxidation of alcohols to the corresponding aldehydes, ketones, or acids, most recently, chromium oxo-species have been used to bring about stoichiometric C–H bond activation of alkanes in the gas phase.<sup>3,4</sup> Further, high-valent compounds of the group 6 elements Cr, Mo, and W are frequently used as catalysts for O-atom transfer from peroxides to organic substrates, e.g., in epoxidation reactions.<sup>5</sup> As to catalytic oxidations, particularly the use of molecular oxygen as a terminal oxidant would be chemically attractive, and, therefore, the generation of high-valent transition-metal oxides using oxygen is of prime interest.<sup>6</sup>

Despite the relevance of transition metals in oxidation processes, the mechanistic details of metal-mediated reactions in the condensed phase remain often unclear, and gas-phase experiments can serve as a helpful complement for mechanistic studies, as they probe directly at a molecular level the elementary steps.<sup>7</sup> The gas-phase oxidation of ethene by  $\text{CrO}_2\text{Cl}^+$  has been

studied by Walba et al. using flow-tube techniques,<sup>8</sup> and it was reported that instead of epoxidation O-atom transfer to the alkene most likely leads to the thermodynamically more stable acetaldehyde. Later, Kang and Beauchamp<sup>9</sup> applied ion-beam techniques in their detailed examination of the reactions of bare  $\text{CrO}^+$  with alkanes and alkenes and found that  $\text{CrO}^+$  behaves somewhat different as compared to the other monoxide cations of first-row transition metals.<sup>10</sup> Recently, O-atom transfer from  $\text{CrO}^+$  to benzene (most likely to yield phenol) has been examined by ion-cyclotron resonance;<sup>11</sup> however, in this study a contribution of electronically excited  $\text{CrO}^+$  could not be ruled out. In addition, the interactions of neutral and charged chromium atoms with dioxygen in solution,<sup>12</sup> in oxygen-doped rare gas matrices<sup>13</sup> as well as in the gas phase,<sup>14,15</sup> and also with respect to theoretical aspects<sup>15b,16</sup> have attracted considerable attention.

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In this article, we present a combined experimental and theoretical study of the  $[\text{Cr}_2\text{O}_2]^+$  system in the gas phase, namely, the chromium(V) dioxide cation  $\text{OCrO}^+$  and the cationic dioxygen complex  $\text{Cr}(\text{O}_2)^+$ . Along with the formation, energetics and electronic states of cationic  $[\text{Cr}_2\text{O}_2]^+$ , we discuss the reactivity of chromium dioxide cation with hydrocarbons and the formation of  $\text{OCrO}^+$  from the ground states of  $\text{Cr}^+$  and  $\text{O}_2$ .<sup>17,18</sup> Some aspects of the  $\text{CrO}_2^-$  anion and the neutral species as well as the dication will be shortly addressed in the context of the cationic species.

## Experimental and Computational Details

The experiments were performed in a tandem mass-spectrometer (Sector-MS) and a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. Because the instrumentation has been described in detail previously, we limit ourselves to the essential aspects.

**Sector-MS.**<sup>19</sup> A modified four-sector tandem mass-spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) was used, in which MS-I is a VG ZAB-HF-2F and MS-II an AMD 604 double focusing mass spectrometer.  $[\text{Cr}_2\text{O}_2]^+$  cations were generated by either electron ionization (EI) of gaseous chromyl chloride  $\text{CrO}_2\text{Cl}_2$  or chemical ionization (CI) of  $\text{Cr}(\text{CO})_6$  with oxygen as reagent gas (ratio ca. 1:50); the latter mixture was also used to generate  $[\text{Cr}_2\text{O}_2]^-$  anions in the negative CI mode. The ions of interest, having 8 keV translational energy, were mass-selected by means of B(1)/E(1) at a mass resolution of  $m/\Delta m \approx 4000$ , and the unimolecular or collision-induced reactions (collision gas: oxygen at 80% transmission, T) occurring in the field-free region between E(1) and B(2) were recorded by scanning B(2). Neutralization-reionization (NR)<sup>20</sup> experiments were performed by colliding B(1)/E(1) mass-selected ions with xenon (80% T), deflecting the remaining ions by applying a potential of 1 kV, reionizing the beam of fast neutrals by collision with oxygen (80% T), and detecting the cationic products by scanning B(2). For the B(1)/E(1) mass-selected  $[\text{Cr}_2\text{O}_2]^-$  anion,  $-\text{NR}^+$  was performed using oxygen in both collision cells (80% T each). Dications were generated by colliding the monocations with oxygen (50–80% T). The energy necessary to remove an electron from a fast moving projectile is taken from its kinetic energy and results in a shift of the dication signal in the kinetic energy scale from the expected E/2 value to a slightly lower one; this energy difference is referred to as the  $Q_{\text{min}}$  value.<sup>21</sup> The  $Q_{\text{min}}$  values were determined by using two different scan modes<sup>22</sup> in which energy scans were done (i) with E(1) for B(1) mass-selected ions and (ii) with E(2) using B(1)/E(1)/B(2) for mass-selection. The reported values are averages of several independent measurements, and within experimental error both methods gave identical results. As references for the calibration of the energy scale,<sup>21a</sup> we used  $\text{Cr}^+$  cation ( $Q_{\text{min}} =$

16.5 eV)<sup>23</sup> and toluene cation radical ( $Q_{\text{min}} = 15.7 \text{ eV}$ )<sup>21a</sup> and applied the multiplicative correction method.<sup>21a</sup> All spectra were accumulated and on-line processed with the AMD/Intectra data system; 5 to 40 scans were averaged to improve the signal-to-noise ratio. *Note that chromyl chloride is not only very poisonous but also heavily oxidizing.* Besides appropriate safety precautions, a pretreating of the inlet system with ozone or chlorine is indicated in order to achieve maximal ion currents.

**FTICR.**<sup>24</sup> These experiments were performed with a *Spectrospin CMS 47X* FTICR mass spectrometer.  $[\text{Cr}_2\text{O}_2]^+$  cations were generated either by EI of  $\text{CrO}_2\text{Cl}_2$  in the external ion source of the instrument or by an ion/molecule reaction of mass-selected  $\text{Cr}(\text{CO})^+$  with oxygen inside the ICR cell;  $\text{Cr}(\text{CO})^+$  was formed by external EI of  $\text{Cr}(\text{CO})_6$ . Externally produced ions were transferred into the analyzer cell which is located within a superconducting magnet (max. field strength 7.05 Tesla).<sup>25</sup> Subsequently, the ions of interest were mass-selected, thermalized by repeated pulses of argon (> 1000 collisions), and mass-selected once more prior to further ion/molecule reactions. Branching ratios and rate constants were derived from the pseudo first-order kinetics and are reported with an error of  $\pm 40\%$ . A detailed report for the complete procedure of calibration of the pressure measurement of the ion gauge forms the subject of a forthcoming paper;<sup>26</sup> in brief, we used a thermal rate constant of  $8.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{Ar}^+$  with  $\text{H}_2$  as the central reference.<sup>27</sup> Under FTICR conditions thermalization of ions generated by EI is much more difficult to achieve as compared to softer ionization methods as CI, FAB, glow discharge, or laser desorption. Besides thermalization with pulsed-in argon, additional quenching with pulsed-in methane (ca. 50 collisions) turned out to be helpful to remove excited  $[\text{Cr}_2\text{O}_2]^+$  cations; however, this procedure is associated with considerable losses of intensity, because  $\text{OCrO}^+$  reacts with methane (see below). As a reasonable compromise between ion intensity and thermalization, quenching with methane prior to the second mass-selection was only performed in the most crucial cases, i.e., the reactions of  $\text{OCrO}^+$  with  $\text{H}_2$ ,  $\text{CH}_4$ , and benzene as well as in the bracketing experiments for determining the ionization energy. Thermalization was assumed to be complete when additional collisions with argon or methane did neither effect rate constants nor branching ratios of the ion/molecule reactions under study. Reagent gases were introduced into the FTICR cell via leak valves at typical pressures of  $4\text{--}40 \times 10^{-9}$  mbar. As will become obvious further below, generation of  $[\text{Cr}_2\text{O}_2]^+$  from  $\text{Cr}(\text{CO})_6/\text{O}_2$  leads to a mixture of different isomers and states of various internal energy contents, and we refrain from a quantification of branching ratios and rate constants for these  $[\text{Cr}_2\text{O}_2]^+$  ions. All data were accumulated and on-line processed using an ASPECT 3000 minicomputer; depending on the ion intensity up to 200 scans were averaged. Due to the high cost of  $^{18}\text{O}_2$  (Campro Scientific), this reagent was only used in the pulsed-valve experiments; therefore, in the comparison of  $^{16}\text{O}/^{18}\text{O}$  exchanges with dioxygen (see below), we reacted  $[\text{Cr}_2^{16}\text{O}_2]^+$  from EI of chromyl chloride with pulsed-in  $^{18}\text{O}_2$ , but  $[\text{Cr}_2^{18}\text{O}_2]^+$  from  $\text{Cr}(\text{CO})^+$  and pulsed-in  $^{18}\text{O}_2$  with leaked-in  $^{16}\text{O}_2$ .

**Calculations.** The ground state and the first excited states of  $\text{CrO}^+$  have been calculated previously in our group<sup>28</sup> using a density functional theory approach.<sup>29</sup> *Ab initio* MO calculations of the  $[\text{Cr}_2\text{O}_2]^+$  system were performed similar to our previous study of the  $[\text{Fe}_2\text{O}_2]^+$  system.<sup>18b</sup> Initially, geometry optimizations of the inserted dioxides  $^2\text{OCrO}^+$  and

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$^4\text{OCrO}^+$  as well as the  $^6\text{Cr}(\text{O}_2)^+$  complex were performed using the approximate density functional theory with the DGAUSS program<sup>30</sup> employing the LCGTO-LSD approach (linear combination of gaussian type orbitals, local spin density); this will be referred to as LSD. All stationary points were characterized as minima or transition structures (TS) on the potential-energy surface by evaluating vibrational frequencies and normal modes using analytical first derivatives and a finite difference scheme for the force-constant matrices. Subsequently, the low lying roots in all spatial and spin symmetries derived from the corresponding fragment asymptotes were computed at the CASPT2D level of theory using atomic natural orbital (ANO) basis sets<sup>31</sup> for oxygen (14s9p4d3f)/[5s4p3d]<sup>31a</sup> and chromium (17s12p9d4f)/[7s6p4d3f];<sup>31b</sup> these basis sets will be referred to as BS-I. Then, the energies of the lowest lying states for all structures were refined at the CASPT2D level using very large ANO basis sets for oxygen (14s9p4d3f)/[5s4p3d2f]<sup>31a</sup> and chromium (21s15p10d6f4g)/[8s7p6d4f2g];<sup>31c</sup> these will be referred to as BS-II. In order to confirm the symmetry breaking in the quartet states of  $\text{OCrO}^+$  (see below), these geometries were reoptimized at the CASSCF level of theory using BS-I. Similarly, the Cr—O—O bond angle of the end-on complex  $\text{Cr}(\text{O}_2)^+$  ( $^6\text{A}''$ ), which is a transition structure with LSD, was scanned in a stepwise manner (10° steps) using the CASPT2D approach with BS-II, and the end-on complex turned out as a minimum at this level of theory. The active molecular orbital space consists mostly of the 4s and 3d orbitals of the metal atom and the 2p orbitals of oxygen (13 electrons in 12 orbitals). All electrons were correlated at the CASPT2D level of theory. The CAS calculations were performed using the MOLCAS (versions 2 and 3) package.<sup>32</sup> Bond dissociation energies (BDEs) were derived from the sum of the energies of the isolated molecules without any further corrections. All computations were performed on either IBM/RS 6000 workstations or a CRAY-YMP computer.

## Results and Discussion

This part is divided into four sections. First, we address the generation and thermochemistry of chromium dioxide cation. Then, we examine the structure of  $[\text{Cr}_2\text{O}_2]^+$  for different spin multiplicities by means of ab initio MO calculations and assign the global minimum and electronic ground states of  $\text{OCrO}^+$  and  $\text{Cr}(\text{O}_2)^+$ . Next, the reactivity of the chromium dioxide cation toward hydrogen and some representative alkanes and alkenes as well as benzene is presented. Finally, we discuss the possible generation of other  $[\text{Cr}_2\text{O}_2]^+$  cations and the dissociation of  $[\text{Cr}_2\text{O}_2]^+$  into  $\text{Cr}^+$  and  $\text{O}_2$  in the context of a chromium-catalyzed oxidation of hydrocarbons with dioxygen as terminal oxidant. In view of the fact that neutral and charged chromium monoxides have formed the subject of several experimental<sup>9,11,33,34</sup> and theoretical investigations,<sup>28,34,35</sup> and neutral and anionic chromium dioxide have also been examined repeatedly,<sup>13–16,36</sup> we adopt the energetics and electronic states of these species from the literature.<sup>37</sup>

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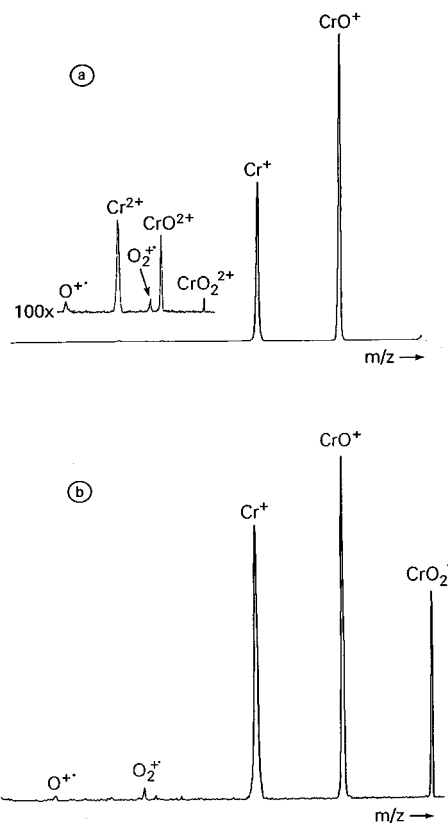
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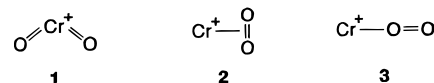
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**Figure 1.** (a) CA mass spectrum ( $\text{O}_2$ , 80% T) of  $[\text{Cr}_2\text{O}_2]^+$  obtained by electron ionization of  $\text{CrO}_2\text{Cl}_2$  and (b) NR mass spectrum (Xe 80% T;  $\text{O}_2$  80% T).

## Scheme 1



**Generation and Thermochemistry of Chromium Dioxide Cation.** The  $[\text{Cr}_2\text{O}_2]^+$  cation can be generated by electron ionization (EI) of chromyl chloride  $\text{CrO}_2\text{Cl}_2$ . Figure 1 shows the collisional activation (CA) and the neutralization reionization (NR) mass spectra of these  $[\text{Cr}_2\text{O}_2]^+$  ions. Both spectra are in line with the structure of an inserted chromium(V) dioxide **1** (Scheme 1).<sup>18b</sup> Upon collisional activation (Figure 1a) sequential losses of oxygen atoms are observed, i.e.,  $\text{CrO}^+:\text{Cr}^+ \approx 2:1$ , while formation of  $\text{O}_2^{2+}$  is almost negligible. In addition,  $\text{CrO}_n^{2+}$  dications ( $n = 0-2$ ) are formed in a charge-stripping process;<sup>21a</sup> note, that the signal for  $\text{CrO}_2^{2+}$  is much weaker than those for  $\text{CrO}^{2+}$  and  $\text{Cr}^{2+}$  (see below). The NR-spectrum (Figure 1b) is dominated by signals for  $\text{CrO}_n^+$  ( $n = 0-2$ ), and the intense recovery signal for  $[\text{Cr}_2\text{O}_2]^+$  indicates that the corresponding neutral is quite stable toward dissociation.<sup>20</sup> Nevertheless, the signal for  $\text{O}_2^{2+}$  in Figure 1b indicates that a certain fraction of the  $[\text{Cr}_2\text{O}_2]^{+/0}$  species underwent dissociation to atomic chromium and dioxygen either in the neutral or the cationic stage via the dioxygen complexes **2** or **3**.

Not surprisingly, the  $[\text{Cr}_2\text{O}_2]^+$  ions generated by EI (70 eV) of  $\text{CrO}_2\text{Cl}_2$  contain a considerable amount of internal energy, and proper thermalization is a prerequisite for the examination

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of the thermochemistry of  $[\text{Cr}_2\text{O}_2]^+$  under FTICR conditions. In order to confirm thorough thermalization of the  $\text{OCrO}^+$  ions by multiple collisions with argon and/or methane (see Experimental Section), we determined the ionization energy (IE) of  $[\text{Cr}_2\text{O}_2]^+$  by the bracketing method in that thermalized  $[\text{Cr}_2\text{O}_2]^+$  is reacted with neutral molecules of known IEs.<sup>37</sup> The observation of an efficient electron transfer from 1,2,3,4-tetrafluorobenzene (IE = 9.5 eV) to  $[\text{Cr}_2\text{O}_2]^+$  and the absence of electron transfer in the presence of hexafluorobenzene (IE = 9.9 eV) imply that  $\text{IE}(\text{CrO}_2) = 9.7 \pm 0.2$  eV.<sup>38</sup> This value is slightly lower than an older value of  $\text{IE}(\text{CrO}_2) = 10.3 \pm 0.5$  eV as determined by appearance energy measurements.<sup>39</sup> However, the reasonable agreement within the error bars together with the fact that our bracketed IE is lower than the previously determined one confirm that the  $[\text{Cr}_2\text{O}_2]^+$  ions are sufficiently thermalized in our experiments. Combining these findings with the experimental number for the heat of formation ( $\Delta H_f$ ) of neutral  $\text{CrO}_2$  ( $-18 \pm 10$  kcal/mol),<sup>40</sup> we arrive at  $\Delta H_f(\text{OCrO}^+) = 206 \pm 15$  kcal/mol, and on the basis of the results of the ion/molecule reactions which will be described below, this figure can be further refined to  $\Delta H_f(\text{OCrO}^+)$  to  $209 \pm 12$  kcal/mol. Finally, the practical absence of  $^{16}\text{O}/^{18}\text{O}$  isotopic exchange of  $^{18}\text{O}_2$  with the  $[\text{Cr}_2\text{O}_2]^+$  cation generated from  $\text{CrO}_2\text{Cl}_2$  is in keeping with a dioxide structure. Moreover, even when the ions were not thermalized at all, electron transfer to yield  $^{18}\text{O}_2^{+}$  prevails, while  $^{16}\text{O}/^{18}\text{O}$ -exchange was observed for less than 1% of the ions, no matter which thermalization procedures were applied.

As far as the connectivity of  $[\text{Cr}_2\text{O}_2]^+$  is concerned, we interpret these findings in that EI of  $\text{CrO}_2\text{Cl}_2$  and subsequent ion thermalization lead to the inserted chromium(V) dioxide cation **1** in its electronic ground state (see below). In the following, we will refer to the ion formed from  $\text{CrO}_2\text{Cl}_2$  as chromium dioxide cation  $\text{OCrO}^+$ .

**Computational Study of the  $[\text{Cr}_2\text{O}_2]^+$  System.** In order to examine the structures of conceivable  $[\text{Cr}_2\text{O}_2]^+$  isomers and the corresponding electronic ground states, we performed a computational study using a combined density functional and ab initio MO approach. As far as connectivities are concerned, the structures **1–3** are feasible, and the spin multiplicities to be considered may range from doublet, quartet, sextet, up to octet states.<sup>41</sup> In general, geometries were optimized using the LSD approach, and the energies were then calculated using the CASPT2D method with the reasonably large basis set BS-I and refined using BS-II. If not stated otherwise, we will refer to the CASPT2D/BS-II//LSD results.

Qualitatively, chromium dioxide cation can be derived by perfect pairing of  $\text{CrO}^+$  with O ( $^3\text{P}$ ). For  $\text{CrO}^+$ , the  $^4\Sigma$  and  $^4\Pi$  states are nearly degenerated and only differ in the occupation of mainly nonbonding orbitals.<sup>28,34,35</sup> Together with the  $^3\text{P}$  ground state of oxygen, we can expect doublet, quartet, and sextet states for the inserted  $\text{OCrO}^+$  cation, and inspection of Tables 1 and 2 reveals that perfect pairing of  $\text{CrO}^+ + \text{O}$  to doublet states of  $\text{OCrO}^+$  is energetically favored. LSD geometry optimization in the doublet state results in a  $C_{2v}$ -symmetrical structure for **1** (Figure 2), and the two short Cr–O distances of

(38) In these particular cases the error of the bracketing method is assumed to be quite low, since no competing reactions occur, i.e., for tetrafluorobenzene only electron transfer takes place and hexafluorobenzene is essentially unreactive toward  $\text{OCrO}^+$ .

(39) Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1961**, *34*, 664.

(40) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (JANAF Tables), p 937.

(41) (a) For a theoretical study of the dioxides of 4d metals, see: Siegbahn, P. E. M. *J. Phys. Chem.* **1993**, *97*, 9096. (b) See also: Bytheway, I.; Hall, M. B. *Chem. Rev.* **1994**, *94*, 639.

**Table 1.** Total Energies (Hartree)<sup>a</sup> of Different Electronic States of  $[\text{Cr}_2\text{O}_2]^+$  Using BS-I and the LSD-Optimized Structures **1** and **2**<sup>a</sup>

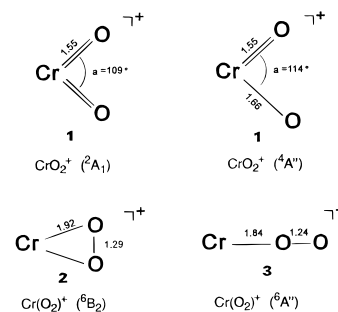
structure	$r_{\text{Cr}-\text{O}(1)}$	$r_{\text{Cr}-\text{O}(2)}$	$r_{\text{O}(1)-\text{O}(2)}$	state	CASSCF	CASPT2D				
<b>1</b> ( $C_{2v}$ )	1.55	1.55	2.51	$^2\text{A}_1$	-1192.94363	-1193.82319				
				$^2\text{B}_1$	-1192.84518	-1193.70362				
				$^2\text{B}_2$	-1192.92351	-1193.81571				
				$^2\text{A}_2$	-1192.87642	-1193.76548				
				$^4\text{A}_1$	-1192.81601	-1193.71668				
				$^4\text{B}_1$	-1192.80719	-1193.71598				
				$^4\text{B}_2$	-1192.83206	-1193.71676				
				$^4\text{A}_2$	-1192.85907	-1193.75827				
				$^6\text{A}_1$	-1192.70319	-1193.58776				
				$^6\text{B}_1$	-1192.65876	-1193.57995				
				$^6\text{B}_2$	-1192.70759	-1193.61124				
				$^6\text{A}_2$	-1192.70261	-1193.60764				
				<b>1</b> ( $C_s$ )	1.55	1.66	2.69	$4\text{A}'$	-1192.87175	-1193.74844
								$4\text{A}''$	-1192.88169	-1193.77139
$^2\text{A}_1$	-1192.81967	-1193.66003								
<b>2</b> ( $C_{2v}$ )	1.92	1.92	1.29	$^4\text{B}_1$	-1192.85590	-1193.72743				
				$^4\text{B}_2$	-1192.81291	-1193.65586				
				$^4\text{A}_2$	-1192.75986	-1193.59598				
				$^6\text{A}_1$	-1192.84087	-1193.71045				
				$^6\text{B}_1$	-1192.86617	-1193.69704				
				$^6\text{B}_2$	-1192.91705	-1193.77036				
				$^6\text{A}_2$	-1192.85636	-1193.71365				
				$^8\text{A}_1$	-1192.56307	-1193.45607				
				$^8\text{B}_1$	-1192.40694	-1193.27279				
				$^8\text{B}_2$	-1192.82806	-1193.70108				
$\text{O}_2$			1.22	$^3\Sigma_g^-$	-149.76068	-150.12478				
				$6\text{S}$	-1043.05930	-1043.64300				
$\text{Cr}^+$										

<sup>a</sup> 1 Hartree = 627.51 kcal/mol.

**Table 2.** Total Energies (Hartree) of the Low-Lying States of  $[\text{Cr}_2\text{O}_2]^+$  Using BS-II for the LSD-Optimized Structures **1–3** and the CASSCF/BS-I-Optimized Geometry of  $\text{OCrO}^+$  ( $^4\text{A}'$  and  $^4\text{A}''$ )

structure	geometry	$r_{\text{Cr}-\text{O}(1)}$	$r_{\text{Cr}-\text{O}(2)}$	$r_{\text{O}(1)-\text{O}(2)}$	state	CASPT2D				
<b>1</b> ( $C_{2v}$ )	LSD	1.55	1.55	2.51	$^2\text{A}_1$	-1194.00127				
					$^2\text{B}_2$	-1193.99664				
					$^4\text{A}_2$	-1193.93611				
<b>1</b> ( $C_s$ )	LSD	1.55	1.66	2.69	$4\text{A}''$	-1193.94846				
					CASSCF <sup>a</sup>	1.55	1.81	3.04	$4\text{A}''$	-1193.95048
					CASSCF <sup>a</sup>	1.55	1.82	3.07	$4\text{A}'$	-1193.94423
<b>2</b> ( $C_{2v}$ )	LSD	1.92	1.92	1.29	$^6\text{B}_2$	-1193.94802				
<b>3</b> ( $C_{\infty v}$ )	LSD <sup>b</sup>	1.84	3.08	1.24	$6\text{A}''^c$	-1193.96295				
$\text{O}_2$	LSD			1.22	$^3\Sigma_g^-$	-150.17523				
$\text{Cr}^+$					$6\text{S}$	-1043.77258				

<sup>a</sup> Geometry optimization at the CASSCF/BS-I level of theory. <sup>b</sup> In order to evaluate the stability of structure **3**, the Cr–O–O bond angle was reoptimized at the CASPT2D level of theory using BS-II, while the bond lengths were fixed to the LSD-geometry of *end-on* complex  $\text{Cr}(\text{O}_2)^+$ ; see text. <sup>c</sup> The  $^6\text{A}''$  state transforms to  $^6\text{B}_2$  in  $C_{2v}$  or to either  $^6\Phi$  or  $^6\Pi$  in  $C_{\infty v}$ .



**Figure 2.** Geometries of the dioxides  $\text{OCrO}^+$  ( $^2\text{A}_1$ ) and  $\text{OCrO}^+$  ( $^4\text{A}''$ ) and the dioxygen complexes  $\text{Cr}(\text{O}_2)^+$  ( $^6\text{B}_2$ ) and  $\text{Cr}(\text{O}_2)^+$  ( $^6\text{A}''$ ) calculated at the LSD/DZP level of theory (bond lengths in Å and bond angles in degree).

1.55 Å are in line with a description of  $\text{OCrO}^+$  ( $^2\text{A}_1$ ) as an chromium(V) dioxide cation with two Cr–O double bonds. The driving force for bending to  $C_{2v}$  can be attributed to the more favorable interaction between the oxygen lone pair electrons

and the half-filled 3d-orbitals of the metal as compared to a linear geometry.<sup>41</sup>

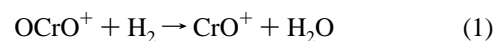
Inserted chromium dioxide cation **1** in the low-spin coupled doublet electronic ground state  ${}^2A_1$  corresponds to the global minimum of the  $[\text{Cr}_2\text{O}_2]^+$  potential-energy surface. However, the  ${}^2B_2$  state is located only slightly higher in energy, such that the accuracy of our computational approach does not allow for a definitive assignment of the ground state symmetry. For the sake of simplicity, in the following we refer to  ${}^2A_1$  as the ground state of  $\text{OCrO}^+$ . The stability of  $\text{OCrO}^+$  ( ${}^2A_1$ ) with respect to dissociation into ground state  $\text{Cr}^+$  ( ${}^6S$ ) and  $\text{O}_2$  ( ${}^3\Sigma_g^-$ ) is calculated as 33.6 kcal/mol. Combining this figure with the experimental heats of formation of  $\text{Cr}^+$  and  $\text{O}_2$ , we arrive at a theoretically predicted  $\Delta H_f^\circ(\text{OCrO}^+)$  of 217 kcal/mol, which is in good agreement with the experimental figure of  $209 \pm 12$  kcal/mol derived above.

The quartet and sextet states of chromium dioxide cation are much higher in energy. The lowest quartet state,  ${}^4A''$ , is 33.2 kcal/mol less stable than  $\text{OCrO}^+$  ( ${}^2A_1$ ) and 0.4 kcal/mol below the  $\text{Cr}^+ + \text{O}_2$  asymptote; all sextet states are very high in energy and were not pursued any further. The origin of the stability difference between the doublet and quartet states of  $\text{OCrO}^+$  arises from the breaking of one double bond by decoupling one electron pair. Qualitatively, the energy difference between these states can be traced back to the difference between ionization of the triplet ground state<sup>14</sup> of neutral  $\text{CrO}_2$  in a bonding  $\pi$ -orbital of a Cr–O double bond and removal of a nonbonding electron from the metal center. Interestingly, the LSD-optimized geometry of  $\text{OCrO}^+$  ( ${}^4A''$ ) is asymmetric with two different Cr–O bond lengths, a typical short one of 1.55 Å and a long one of 1.66 Å. In terms of molecular orbital theory, symmetry breaking from  $C_{2v}$  to  $C_s$  is somewhat unexpected, because in the  $C_{2v}$  point group there exist no degenerate orbitals which could give rise to spontaneous symmetry breaking, e.g., Jahn-Teller or Renner-Teller effects. Although we cannot exclude that the asymmetry of  $\text{OCrO}^+$  ( ${}^4A''$ ) is an artifact of our computational approach, it has also been argued<sup>42</sup> that excited  $\text{SO}_2$  undergoes the transition  $C_{2v} \rightarrow C_s$ . Notwithstanding these arguments, the  $C_s$  structure of  $\text{OCrO}^+$  ( ${}^4A''$ ) is perfectly in line with the valence bond description of this isomer by localized single and double bonds. In order to verify that the LSD computed geometries are not an artifact of the single reference approach, these quartet states were also geometry optimized using CASSCF/BS-I. At this level of theory, again bent  $C_s$ -symmetrical structures were obtained, and the differences of the Cr–O bond lengths are even more pronounced, i.e.,  $\Delta r_{\text{Cr-O}} = 0.26$  Å for both states. Using these geometries for CASPT2D/BS-II calculations has only minor influence on the computed energetics in that  $\text{OCrO}^+$  ( ${}^4A''$ ) is 1.7 kcal/mol lower in energy than separated  $\text{Cr}^+$  and  $\text{O}_2$  and still favored over  $\text{OCrO}^+$  ( ${}^4A'$ ).

Quite a different order of stabilities for the various spin multiplicities is found for the side-on and end-on  $\text{Cr}(\text{O}_2)^+$  complexes (structures **2** and **3**). In general, ground state chromium cation ( ${}^6S$ ) and ground state dioxygen ( ${}^3\Sigma_g^-$ ) can give rise to octet, sextet, and quartet states for  $\text{Cr}(\text{O}_2)^+$ . The LSD geometry optimization for the sextet complex reveals a side-on minimum with structure **2**, whereas the end-on structure **3** displays an imaginary frequency of  $i143$   $\text{cm}^{-1}$  for bending of the  $\text{O}_2$  unit. The energetically lowest-lying state is  $\text{Cr}(\text{O}_2)^+$  ( ${}^6B_2$ )

in which two electrons, one of Cr and one of  $\text{O}_2$ , undergo spin coupling. States of other spatial symmetries as well as the octet and quartet states are much higher in energy and can therefore not account for complex formation between  $\text{Cr}^+$  and  $\text{O}_2$ . However, at the CASPT2D/BS-I/LSD level of theory even for  $\text{Cr}(\text{O}_2)^+$  ( ${}^6B_2$ ) the dissociation energy of the  $\text{Cr}^+-\text{O}_2$  bond is calculated to be as small as 1.7 kcal/mol and decreases to only 0.1 kcal/mol with BS-II (Table 2), a result which is not reasonable for the complexation of the polarizable oxygen molecule by a metal cation. The small imaginary frequency of the end-on structure **3** indicates a flat potential-energy surface for the complex and led us to examine the end-on structure at a higher level of theory. Actually, using the CASPT2D/BS-II/LSD approach the end-on complex **3** is calculated to be 9.5 kcal/mol more stable than the side-on species **2**. In addition, a scan of the Cr–O–O bond angle at this level of theory reveals the linear end-on complex **3** as the minimum, even though the potential of the  ${}^6A''$  surface is quite flat with respect to the bending mode. These results can be rationalized by considering the electronic prerequisites: Ground state  $\text{Cr}^+$  ( ${}^6S$ ) has a  $3d^5$  high-spin configuration and an empty 4s shell. Formation of a covalent bond is most favored through spin-pairing of a  $\text{Cr}^+$  3d electron with the in-plane  $\pi^*$  electron of side-on dioxygen leading to the sextet  $\text{Cr}(\text{O}_2)^+$  with structure **2**. However, the small radial extent of the compact 3d shell results in an small overlap with  $\text{O}_2$  and the large exchange-energy losses upon distortion of the half filled high-spin  $3d^5$  configuration of  $\text{Cr}^+$  ( ${}^6S$ ) disfavor this type of bonding. Consequently, simple complex formation by donation of charge from the  $\text{O}_2$  ligand to  $\text{Cr}^+$  favors the end-on structure **3** due to the larger polarizability of dioxygen along the O–O bonding axes. Actually, both types of bonding are involved to some extent in  ${}^6\text{Cr}(\text{O}_2)^+$  as indicated by (i) the sextet multiplicity and (ii) the relatively weakly bound end-on structure with a small bending force constant. In fact, as the LSD level of theory is known to underestimate exchange-energy losses and to overestimate the covalent contributions,<sup>43</sup> in a borderline case like  ${}^6\text{Cr}(\text{O}_2)^+$  the wrong side-on structure is predicted to correspond to the minimum, in contradiction to the CASPT2D results. Thus, even though LSD geometries are usually reasonable starting points for energy calculations, caution is indicated in problematic cases bearing low-lying frequencies.

**Reactivity of Ground State  $\text{OCrO}^+$ .** Formally, chromium dioxide cation  ${}^2\text{OCrO}^+$  represents a high-valent chromium(V) compound. Therefore, it is not unexpected that the thermalized  $\text{OCrO}^+$  cation generated by EI of  $\text{CrO}_2\text{Cl}_2$  oxidizes hydrocarbons quite efficiently. In fact, under FTICR conditions even dihydrogen is activated by  $\text{OCrO}^+$  to yield  $\text{CrO}^+$  and water (reaction 1).



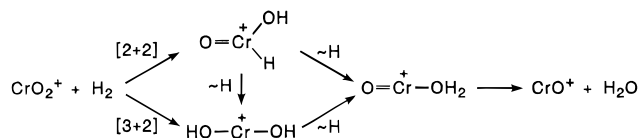
According to the thermochemistry of  ${}^2\text{OCrO}^+$  outlined above, the exothermicity of reaction 1 amounts to ca. 43 kcal/mol. However, the experimentally measured rate constant of  $k_R = 9.8 \times 10^{-12}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> is rather low as compared to the capture rate constant  $k_C = 1.5 \times 10^{-9}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> as derived from gas kinetic theory.<sup>44</sup> Thus, the reaction efficiency  $\phi$  (defined as  $\phi = k_R/k_C$ ) amounts to only about 0.007 for the reaction of  $\text{OCrO}^+$  with hydrogen and 0.004 for deuterium, respectively. In order to ensure ion thermalization, argon and methane were pulsed-in repeatedly prior to mass-selection of  $\text{OCrO}^+$ , and its reaction with hydrogen was followed

(42) (a) Herzberg, G. *Molecular Spectra and Molecular Structure*; Krieger, Malabar, 1991; Vol. 3, p 605. (b) For a related example of  $C_s$  symmetry in the  $[\text{Cu}_2\text{O}_2]$  system, see: Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H.; Sodupe, M. J. *Phys. Chem.* **1993**, *97*, 856. (c) See also: Wu, H.; Desai, S. R.; Wang, L.-S. *J. Chem. Phys.* **1995**, *103*, 4363. (d) Also the excited quartet state  $\text{W}(\text{O})_2^+$  ( ${}^4A'$ ) has  $C_s$ -symmetry: Ferhati, A.; Ohanessian, G., Paris, personal communication.

(43) Ziegler, T.; Li, J. *Can. J. Chem.* **1994**, *72*, 783.

(44) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.

## Scheme 2



until almost complete conversion (i.e., >99%) in the presence of a 4-fold excess of argon as a buffer gas. In these experiments, we found no deviation from strict first-order kinetics, even though at high conversions of  $\text{OCrO}^+$  also many thermalizing collisions with hydrogen occurred prior to each reactive one. As discussed in a previous publication,<sup>45</sup> for reactive metal-oxide cations the determination of very low rate constants can be associated with experimental errors, in particular with respect to the purity of the reagents and background contaminants. In fact, we observe that (i) the  $\text{CrO}^+$  cation formed in reaction 1 is slowly converted into  $\text{Cr}^+$ , although thermalized  $\text{CrO}^+$  does not react with  $\text{H}_2$ ,<sup>9,46</sup> and (ii) small amounts of other products appear at long reaction times, e.g. 1%  $[\text{Cr}, \text{C}_2, \text{H}_4, \text{O}]^+$  at 99.5% conversion of the  $\text{OCrO}^+$  precursor. Thus, we conclude that background hydrocarbons are present in the vacuum system, and, therefore, the rate constant of  $9.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for reaction 1 as determined from the disappearance of  $\text{OCrO}^+$  can be slightly too high. Further, these sources of error as well as the accuracy of the pressure measurement<sup>26</sup> do not allow for a precise quantitative analysis of the different efficiencies for  $\text{H}_2$  and  $\text{D}_2$  in terms of an intermolecular kinetic isotope effect, except for the qualitative finding that the isotope effect is quite small.<sup>47</sup> Despite these uncertainties, the fact that reaction 1 occurs for thermalized ions is beyond any doubt.

The ion/molecule reaction of  $\text{OCrO}^+$  with hydrogen is also of interest from a fundamental point of view: As derived above,  $\text{OCrO}^+$  exhibits a doublet ground state. However, the quoted enthalpy of reaction 1 would require that  $\text{CrO}^+$  is formed in its quartet ground state (either  $^4\Sigma^+$  or  $^4\Pi$ ),<sup>34</sup> while the spin-allowed formation of  $\text{CrO}^+$  ( $^2\Delta$ ) is ca. 30 kcal/mol less exothermic.<sup>35b</sup> Though the spin-allowed formation of  $\text{CrO}^+$  ( $^2\Delta$ ) would still be thermochemically possible, the low efficiency of reaction 1 and the small kinetic isotope effect imply that the reaction involves curve crossing from the doublet to the quartet surface via spin-orbit coupling as a central step in the reaction coordinate en route to product formation.<sup>35b</sup> This analysis is analogous to the recently studied oxidation of molecular hydrogen by bare  $\text{FeO}^+$  cation.<sup>26,28,47,48</sup>

With respect to the reaction mechanism, two different scenarios are conceivable (Scheme 2): After formation of the adduct complex  $[\text{OCrO}^+ \cdot \text{H}_2]$ , either addition of the H–H unit across a single Cr–O unit ([2 + 2] pathway) or a simultaneous reaction involving both oxygen termini ([3 + 2] pathway) can occur.<sup>4</sup> The [2 + 2] pathway leads to  $\text{OCr}(\text{H})(\text{OH})^+$  which can then undergo H-migration from the metal to the oxygen atom to yield  $\text{Cr}(\text{OH})_2^+$  or to the hydroxy group to form the oxo complex  $(\text{H}_2\text{O})\text{CrO}^+$ . The chromium dihydroxide cation  $\text{Cr}(\text{OH})_2^+$  may serve as an intermediate in both pathways and most probably, this formal chromium(III) compound exhibits a

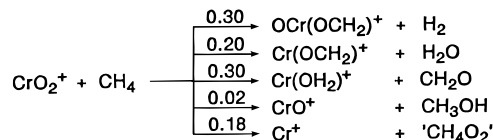
(45) Ryan, M. F.; Fiedler, A.; Schröder, D.; Schwarz, H. *Organometallics* **1994**, *13*, 4072.

(46) An alternative explanation for the subsequent formation of  $\text{Cr}^+$  may assume that  $\text{CrO}^+$  is formed in an excited state, e.g.  $\text{CrO}^+$  ( $^2\Delta$ ), which reacts with hydrogen. Alternatively, due to the large reaction exothermicity, the  $\text{CrO}^+$  ions may be formed in excited rovibronic states. As we cannot discriminate between these two possibilities, we have not further attempted to resolve this issue.

(47) Schröder, D.; Fiedler, A.; Ryan, M. F.; Schwarz, H. *J. Chem. Phys.* **1994**, *98*, 68.

(48) Clemmer, D. E.; Chen, Y.-M.; Khan, F. A.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 6522.

## Scheme 3



quartet ground state in analogy to  $\text{Cr}(\text{CH}_3)_2^+$  ( $^4\text{B}_2$ ).<sup>49</sup> Thus, if spin-inversion takes place in reaction 1, it is likely to occur at this point, i.e.,  $^2\text{OCrO}^+ + \text{H}_2 \rightarrow ^2\text{Cr}(\text{OH})_2^+ \rightarrow ^4\text{Cr}(\text{OH})_2^+ \rightarrow ^4\text{CrO}^+ + \text{H}_2\text{O}$ . Subsequently, isomerization leads to  $^4(\text{H}_2\text{O})\text{-CrO}^+$  and finally spin-allowed dissociation into the ground state products  $\text{CrO}^+$  ( $^4\Sigma^+$  or  $^4\Pi$ ) and  $\text{H}_2\text{O}$  ( $^1\text{A}_1$ ).<sup>50</sup>

As compared to reaction 1, the oxidation of methane with  $\text{OCrO}^+$  is more efficient ( $\phi = 0.12$ ), i.e.,  $k_R = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_C = 1.0 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The  $\text{OCrO}^+/\text{CH}_4$  couple necessarily involves spin inversion en route to product formation, because most of the products (Scheme 3) have ground states of higher multiplicities with rather large excitation energies to the doublet surface, e.g. 3.8 eV for the excitation  $\text{Cr}^+$  ( $^6\text{S}$ )  $\rightarrow$   $\text{Cr}^+$  ( $^2\text{D}$ ). The losses of neutral  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{O}$ , and “ $\text{CH}_4\text{O}_2$ ” (most probably in form of  $\text{H}_2\text{O} + \text{CH}_2\text{O}$ ) are not surprising and can be explained to proceed via the bisligand complex  $(\text{H}_2\text{O})\text{Cr}(\text{OCH}_2)^+$  as a common intermediate (see below). The key product is the loss of dihydrogen to yield the  $[\text{Cr}, \text{C}, \text{H}_2, \text{O}_2]^+$  product ion. Because previous studies have demonstrated that formaldehyde may undergo  $\text{Cr}^+$ -mediated dehydrogenation to the corresponding carbonyl complex,<sup>51a</sup> one is tempted to assign an analogous  $(\text{H}_2\text{O})\text{Cr}(\text{CO})^+$  structure to this product ion and attribute its formation to a subsequent degradation of the formaldehyde ligand in  $(\text{H}_2\text{O})\text{Cr}(\text{OCH}_2)^+$ . However, the secondary reaction of the  $[\text{Cr}, \text{C}, \text{H}_2, \text{O}_2]^+$  product ion with background water rules out this conjecture in that formation of  $[\text{Cr}, \text{H}_2, \text{O}_2]^+$  takes place; a process which formally represents an exchange reaction in which water substitutes a formaldehyde ligand in  $[\text{Cr}, \text{C}, \text{H}_2, \text{O}_2]^+$ . Further, irrespective of the isotopic composition of the  $[\text{Cr}, \text{C}, \text{H}_{2-n}, \text{D}_n, \text{O}_2]^+$  ions ( $n = 0-2$ ) generated in the reactions of  $\text{OCrO}^+$  with  $[\text{D}_2]$ - and  $[\text{D}_4]$ -methane,  $[\text{Cr}, \text{H}_2, \text{O}_2]^+$  is the only secondary product and the complete label is lost in the neutral. These findings suggest that the  $[\text{Cr}, \text{C}, \text{H}_2, \text{O}_2]^+$  ion corresponds to a formaldehyde complex of chromium oxide, i.e.,  $\text{OCr}(\text{OCH}_2)^+$ . At first sight, the formation of this ion is quite surprising, because it combines a reactive metal-oxo moiety with an oxidizable aldehyde ligand. However, similar reactions of only one of two oxo-ligands have been previously proposed in the reactions of  $\text{OsO}_2^+$  with methane and  $\text{CrO}_2\text{Cl}^+$  with ethylene.<sup>8,52</sup> Finally, the very minor product channel to yield  $\text{CrO}^+$  and methanol is of interest for thermochemical reasons, because its occurrence can be used for the refinement of the  $\Delta H_f(\text{OCrO}^+)$  figure as mentioned above.

It is now well-accepted<sup>10</sup> that in the C–H bond activation of an alkane R–H by a reactive metal oxide  $[\text{M}]\text{O}$  ( $[\text{M}]$  = ligated or bare transition metal) the formation of an O–H bond provides the driving force for further reactions such that R is initially attached to  $[\text{M}]$ . This conjecture is also in line with simple thermochemical considerations, since the strength of an O–H bond exceeds that of an O–C bond, and vice versa, for coordinatively unsaturated species often  $[\text{M}]$ –C bonds are

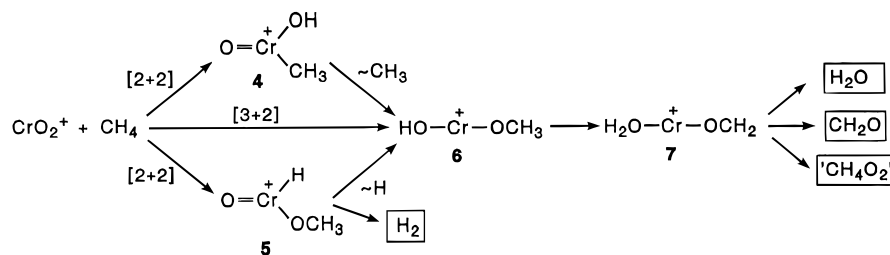
(49) Rosi, M.; Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1990**, *94*, 8656.

(50) For the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Cr}^+$ , see: Schalley, C. A.; Wesendrup, R.; Schröder, D.; Schwarz, H. *Organometallics* **1996**, *15*, 678.

(51) (a) Schalley, C. A.; Wesendrup, R.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1995**, *117*, 7711. (b) Wesendrup, R.; Schalley, C. A.; Schröder, D.; Schwarz, H. *Chem. Eur. J.* **1995**, *1*, 608.

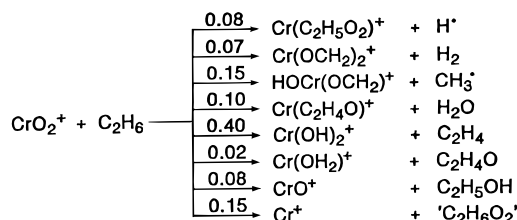
(52) Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 75.

## Scheme 4



stronger than  $[\text{M}]-\text{H}$  bonds.<sup>37,53</sup> Thus, an addition of  $\text{R}-\text{H}$  across an  $[\text{M}]-\text{O}$  bond is much more likely to yield an insertion intermediate  $\text{R}-[\text{M}]-\text{OH}$  than the isomeric  $\text{H}-[\text{M}]-\text{OR}$  species; both can then undergo either reductive elimination of the corresponding alcohol  $\text{ROH}$  or further reactions. The formation of  $\text{OCr}(\text{OCH}_2)^+$  from  $\text{OCrO}^+/\text{CH}_4$  is also telling with regard to the reaction mechanism: In fact, dehydrogenation is hardly conceivable involving an initial formation of  $\text{H}_3\text{C}-\text{Cr}(\text{O})-\text{OH}^+$ , **4**, (Scheme 4), because once a (strong)  $\text{O}-\text{H}$  bond is formed, it is unlikely to be broken again in favor of the dehydrogenation process. However, when  $\text{C}-\text{H}$  bond activation of methane by  $\text{OCrO}^+$  involves  $\text{H}-\text{Cr}(\text{O})-\text{OCH}_3^+$ , **5**, as the first intermediate,  $\beta$ -hydrogen transfer from the methoxy group together with loss of molecular hydrogen becomes a feasible option.<sup>7a,54,55</sup> While this type of addition has rarely been observed for transition-metal monoxide cations,<sup>10</sup> a similar reversal of the regioselectivity for  $\text{R}-\text{H}$  addition across the  $\text{Fe}-\text{O}$  bond has been reported in the reaction of the formal iron(IV) compound  $\text{OFeOH}^+$  with methane.<sup>56</sup> A different behavior of  $\text{OCrO}^+$  as compared to other transition-metal monoxide cations is also in keeping with the observation that the intramolecular kinetic isotope effect associated with  $\text{C}-\text{H}/\text{D}$  bond activation of  $\text{CH}_2\text{D}_2$  is rather small ( $k_{\text{H}}/k_{\text{D}} \approx 1.6$ )<sup>57</sup> as compared to cationic transition-metal monoxides.<sup>10</sup> Further, the involvement of **5** as an intermediate suggests that, at least in part, bond activation of methane by  $\text{OCrO}^+$  involves only a single  $\text{O}$ -atom in terms of a  $[2+2]$  cycloaddition, and similar arguments apply for the formation of  $\text{CrO}^+$ . There also exists an electronic reasoning for the  $[2+2]$  pathway in the reactions of  $^2\text{OCrO}^+$ . The initial insertion products **4** and **5** are likely to exhibit doublet ground states, because four of the five  $3d$  electrons of  $\text{Cr}^+$  are involved in covalent bonds such that one uncoupled electron is left behind. Thus, the  $[2+2]$  route conserves the spin of the reactants. In contrast, the  $[3+2]$  pathway leads directly to **6** which is likely to exhibit a quartet ground state. Hence, in this route the bond formation and curve crossing must occur simultaneously along the reaction coordinate. Finally, the formaldehyde ligand in  $\text{OCr}(\text{CH}_2\text{O})^+$  may lower the splitting of  $1.2 \text{ eV}$ <sup>5b</sup> between the doublet and quartet states of  $\text{CrO}^+$ , such that the  $\text{OCr}(\text{OCH}_2)^+$

## Scheme 5



product might retain doublet spin. As a consequence, spin-conservation would allow for the formation of  $\text{OCr}(\text{CH}_2\text{O})^+$ , while the other product channels have to circumvent the spin-inversion bottleneck; while this is less effective, it certainly takes place, e.g. for thermochemical reasons the formation of  $\text{Cr}^+$  ( $^2\text{D}$ ) is impossible.

The other reaction products can be formed by either  $\text{CH}_3$ -transfer from the metal to the oxygen (**4**  $\rightarrow$  **6**), likewise via  $\text{H}$ -transfer (**5**  $\rightarrow$  **6**), or—though less likely—by an addition of the  $\text{R}-\text{H}$  bond to the oxygen termini of  $\text{OCrO}^+$  in terms of a  $[3+2]$  cycloaddition which leads directly to **6**. The latter ion **6** then serves as an intermediate which can undergo hydrogen transfer from the methoxide unit to the hydroxy ligand (either via the metal or directly to the oxygen atom)<sup>55</sup> to yield the bisligated complex  $(\text{H}_2\text{O})\text{Cr}(\text{OCH}_2)^+$  **7** from which formaldehyde and/or water are lost eventually.

Not surprisingly, the reaction efficiencies  $\phi_i$  of  $\text{OCrO}^+$  with higher alkanes increase as compared to those for dihydrogen and methane (i.e.,  $\phi(\text{C}_2\text{H}_6) = 0.5$ ,  $\phi(\text{C}_3\text{H}_8) = 0.7$ ,  $\phi(i\text{-C}_4\text{H}_{10}) = 0.6$ ). In general, the product patterns of the ion/molecule reactions of  $\text{OCrO}^+$  with larger alkanes are more complex. This is due to the fact that the more  $\text{C}-\text{H}$  bonds and possible intermediates become available, the more reaction pathways compete with each other.<sup>10</sup> For the sake of clarity, we only discuss those pathways in some more detail in which principally new features or reaction mechanisms evolve. Further, not all product ions were structurally characterized, and the formulas given should only be viewed as reasonable suggestions based on similar reactions of other transition-metal ions.<sup>7,10</sup> Let us illustrate the decrease in selectivity by discussing the reaction of  $\text{OCrO}^+$  with ethane (Scheme 5): (i) The losses of  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_4\text{O}$ ,  $\text{C}_2\text{H}_6\text{O}$ , and “ $\text{C}_2\text{H}_6\text{O}_2$ ” are analogous to the processes observed in the  $\text{OCrO}^+/\text{CH}_4$  couple and can be explained by invoking the higher homologues of **4**–**7**. (ii) Homolytic bond cleavages lead to the eliminations of  $\text{H}^*$  as well as  $\text{CH}_3^*$ , most likely from the intermediate  $[\text{HO}-\text{Cr}-\text{OC}_2\text{H}_5]^+$  **10**, to form the corresponding aldehyde complexes of  $\text{CrOH}^+$ . (iii) A new pathway which is not possible in the reactions of  $\text{H}_2$  and  $\text{CH}_4$  leads to the generation of  $\text{Cr}(\text{OH})_2^+$  concomitant with the loss of neutral alkene. The latter channel can proceed via initial  $\text{C}-\text{H}$  bond activation of ethane to yield the insertion intermediate **8**, subsequent transfer of a  $\beta$ -hydrogen atom from the ethyl group to the  $\text{OCrOH}$  unit (**8**  $\rightarrow$  **9**) and terminating loss of the ethene ligand (Scheme 6). Alternatively, **10** may undergo  $\text{C}-\text{O}$  bond cleavage and electron transfer (ET) in the complex to an

(53) Martinho Simões, J. A.; Beauchamp J. L. *Chem. Rev.* **1990**, *90*, 629.

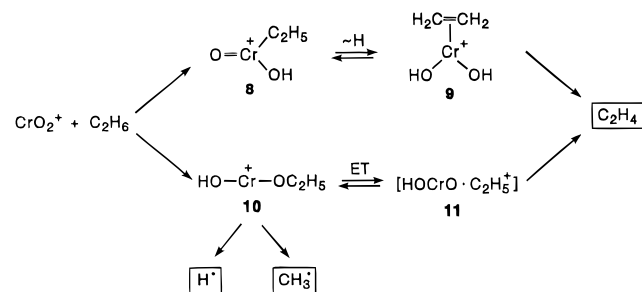
(54) (a) Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320. (b) Cassady, C. J.; Freiser, B. S.; McElvany, S. W.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 6125. (c) Fiedler, A.; Schröder, D.; Schwarz, H.; Tjelta, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1996**, *118*, 5047.

(55) Most likely, the hydrogen atom from the methoxy group is directly transferred to the other hydrogen in **5** without involving a dihydrido-metal intermediate; see: (a) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2282. (b) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *J. Phys. Chem.* **1996**, *100*, 6236.

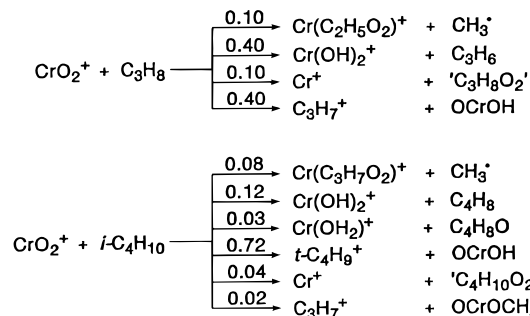
(56) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 991.

(57) The isotope effect was determined for the  $\text{OCrO}^+/\text{CH}_2\text{D}_2$  couple as an average of the isotopologous products formed according to Scheme 3. A precise evaluation of the individual effects for losses of water and formaldehyde was hampered by (i) rapid  $\text{H}/\text{D}$ -exchange of  $\text{Cr}(\text{OD}_2)^+$  and  $\text{Cr}(\text{ODH})^+$  with background water and (ii) accidental mass-overlap of  $\text{Cr}(\text{OCD}_2)^+$  with the  $\text{OCrO}^+$  precursor ion.

## Scheme 6



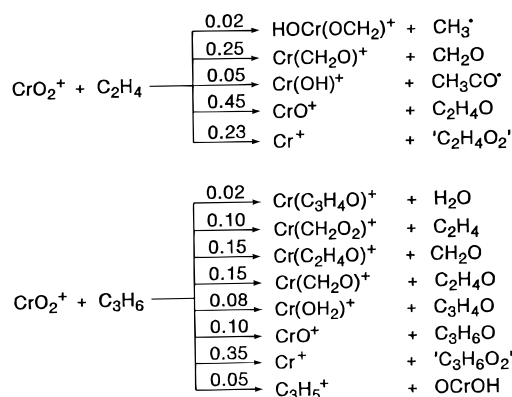
## Scheme 7



intermediate that formally contains a carbocation (**10** → **11**) and which can lead to  $\text{Cr}(\text{OH})_2^+$  via proton transfer; note that proton transfer from  $\text{Cr}(\text{OH})_2^+$  to ethylene (proton affinity, PA = 163 kcal/mol)<sup>58</sup> to yield neutral  $\text{OCrOH}$  and an ethyl cation is not observed experimentally. In the context of a recent study of the related ion/molecule reaction of  $\text{Cr}^+$  with dimethylperoxide,<sup>51</sup> we argued that the absence of  $\text{C}_1$ -products such as losses of  $\text{CH}_n\text{O}$  ( $n = 2-4$ ) indicates that direct C–C bond cleavage in terms of a [3 + 2] cycloaddition to yield the insertion intermediate  $(\text{H}_3\text{CO})_2\text{Cr}^+$  does not occur in the  $\text{OCrO}^+/\text{C}_2\text{H}_6$  couple. In contrast, a bismethoxy chromium cation constitutes the central intermediate en route to the  $\text{Cr}^+$ -mediated decomposition of dimethylperoxide. Thus, we conclude that  $\text{OCrO}^+$  exhibits a strong preference for C–H bond activation of alkanes and that C–C bond activation via the [3 + 2] route does not take place.

In the  $\text{OCrO}^+/\text{C}_3\text{H}_8$  couple (Scheme 7) most of the pathways observed for  $\text{OCrO}^+/\text{C}_2\text{H}_6$  are by and large suppressed in favor of two major product channels to yield  $\text{Cr}(\text{OH})_2^+$ , together with neutral  $\text{C}_3\text{H}_6$ , and  $\text{C}_3\text{H}_7^+$  concomitant with neutral  $\text{OCrOH}$ . As to the reaction mechanism the formation of  $\text{C}_3\text{H}_7^+$  can be traced back to the stability of the isopropyl cation. Due to the similar intensities of  $\text{Cr}(\text{OH})_2^+$  and  $\text{C}_3\text{H}_7^+$  as well as with respect to the fact that these two channels are conceivably connected via a proton transfer, we describe the product distribution in terms of an acid–base equilibrium between  $\text{Cr}(\text{OH})_2^+ + \text{C}_3\text{H}_6$  and  $\text{OCrOH} + \text{C}_3\text{H}_7^+$ .<sup>59</sup> To a first approximation, we estimate that the PA of neutral oxo-chromium hydroxide  $\text{OCrOH}$  is similar to that of propene (PA = 180 kcal/mol). This interpretation is substantiated by the reaction of  $\text{OCrO}^+$  with isobutane, in which the formation of *tert*-butyl cation and neutral  $\text{OCrOH}$  prevails by and large, while the complementary products  $\text{Cr}(\text{OH})_2^+ + \text{C}_4\text{H}_8$  are much less abundant. This finding agrees well with the proposal that  $\text{PA}(\text{OCrOH})$  is smaller than that of isobutene (PA = 196 kcal/mol). The other products in the reactions of  $\text{OCrO}^+$  with propane and isobutane are in keeping with the

## Scheme 8



mechanisms proposed for the activation of methane and ethane. The reduced complexity of the product distribution as compared to the  $\text{OCrO}^+/\text{C}_2\text{H}_6$  couple does, however, not imply an increase of intrinsic selectivity, rather, it is a consequence of the predominating channels leading to either  $\text{Cr}(\text{OH})_2^+$  or carbocations. Finally, the formation of  $\text{C}_3\text{H}_7^+$  in the reaction of  $\text{OCrO}^+$  with isobutane indicates that besides formal  $\text{H}^-$ -transfer from the alkane to  $\text{OCrO}^+$  also  $\text{H}_3\text{C}^-$ -transfer is thermochemically allowed.

In order to examine the reactivity of  $\text{OCrO}^+$  with unsaturated hydrocarbons, we have chosen ethene, propene, and benzene as model compounds. In the reaction of ethene with  $\text{OCrO}^+$  ( $\phi = 0.5$ ) three main products are formed and two minor channels (<5%) lead to losses of  $\text{CH}_3^+$  and  $\text{CH}_3\text{CO}^+$  radicals (Scheme 8). The major reaction products can be rationalized by initial attack of  $\text{OCrO}^+$  to the C–C double bond in terms of a [2 + 2] cycloaddition to form the metallaoxetane **12** (Scheme 9).<sup>5b</sup> Subsequently, the primary intermediate **12** can either rearrange to the five-membered ring **13** which then undergoes loss of one or two formaldehyde units.<sup>60</sup> In competition, a metal-assisted 1,2-hydrogen migration<sup>5b,9,61</sup> may lead to the acetaldehyde/ $\text{CrO}^+$  complex **14**, which subsequently splits off  $\text{CH}_3^+$ ,  $\text{CH}_3\text{CO}^+$ , and  $\text{C}_2\text{H}_4\text{O}$ ; the latter most likely corresponds to acetaldehyde. Although we cannot rigorously exclude that a [3 + 2] cycloaddition leads directly to **13**, the generation of methyl and acetyl radicals provides strong evidence for the operation of a [2 + 2] mechanism, because the [3 + 2] pathway should lead to almost exclusive elimination of one or two formaldehyde molecules from **13** without any further rearrangement prior to fragmentation. Further, the preference for the [2 + 2] type of addition is also in accord with the findings outlined above for the reactions of the alkanes.<sup>62</sup> The reaction of  $\text{OCrO}^+$  with propene occurs close to the collision limit ( $\phi = 0.8$ ), and a large variety of products is formed which we have not attempted to characterize further. The complexity of reaction products can be attributed to competition between activation of the C–C double bond of the alkene and C–H bond activation in the allylic position; the latter process is particularly demonstrated by formal hydride transfer from propene to  $\text{OCrO}^+$  to yield the allyl cation concomitant with neutral  $\text{OCrOH}$ . In fact, the decrease in selectivity in going from ethene to propene reveals a general dilemma in the oxidation of substituted alkenes

(60) We cannot exclude that  $\text{CH}_2\text{O}$  loss leads to  $\text{OCr}(\text{CH}_2)^+$  instead of the proposed structure  $\text{Cr}(\text{OCH}_2)^+$  and have not attempted to further characterize this product.

(61) (a) Fisher, E. R.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 1674. (b) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1431.

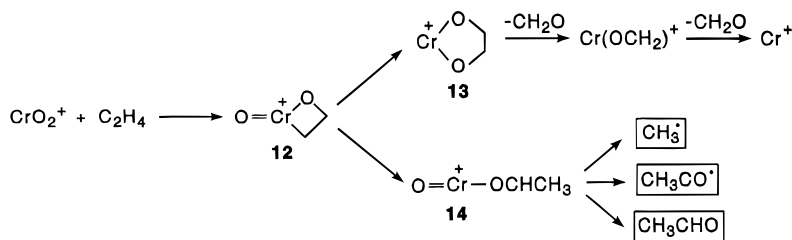
(62) For recent discussions of [2 + 2] versus [3 + 2] pathways in the reactions of osmium(VIII) compounds with alkenes, see: (a) Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 4937. (b) Norrby, P.-O.; Kolb, H. C.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 8470.

(58) Proton affinities were taken from: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

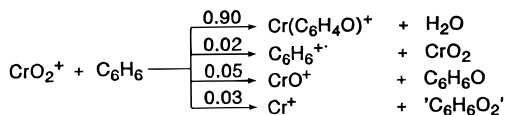
(59) For a related behavior of  $\text{Fe}^+$  complexes, see: Schröder, D.; Wesendrup, R.; Schalley, C. A.; Zummack, W.; Schwarz, H. *Helv. Chim. Acta* **1996**, *79*, 123.



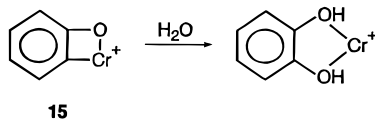
## Scheme 9



## Scheme 10



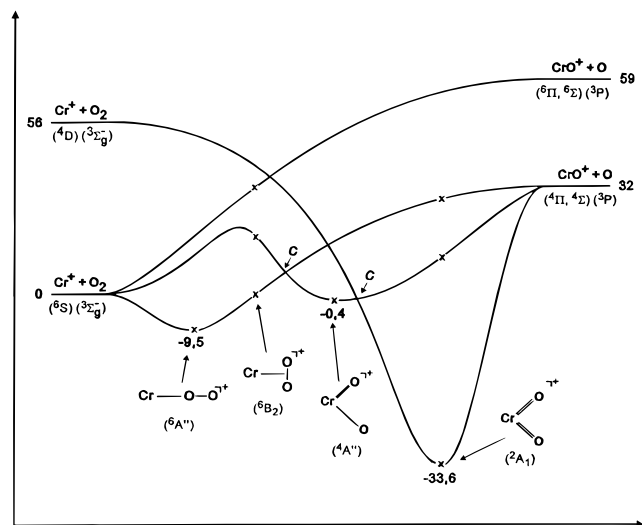
## Scheme 11



by oxidants on the basis of high-valent transition-metal oxides, in that the latter are often too reactive to allow for a discrimination between activation of a C–C double bond and allylic C–H bonds.<sup>63</sup> Obviously, this lack of reactivity also holds true for  $\text{OCrO}^+$ , and only appropriate tuning of the reactivity by means of ligand effects may bring about more selective pathways for the oxidation of alkenes.<sup>64</sup>

In the reaction of  $\text{OCrO}^+$  with benzene ( $\phi = 1.0$ ) dehydration to yield  $[\text{Cr}_2\text{C}_6\text{H}_4\text{O}]^+$  dominates, while formation of  $\text{Cr}^+$ ,  $\text{CrO}^+$ , and electron transfer from benzene (IE = 9.25 eV) to  $\text{OCrO}^+$  can hardly compete (Scheme 10). Considering the IE( $\text{CrO}_2$ ) = 9.7 ± 0.2 eV as derived above, the low intensity of electron transfer with benzene demonstrates once more that C–H bond activation by  $\text{OCrO}^+$  is very efficient and can almost suppress electron transfer. We can merely speculate about the reaction mechanism,<sup>65</sup> but the intense dehydration process demonstrates that  $\text{OCrO}^+$  can bring about the C–H bond activation of benzene, although C–H bonds of arenes are among the strongest ones.<sup>37</sup> A number of structures are conceivable for the  $[\text{M}_2\text{C}_6\text{H}_4\text{O}]^+$  species,<sup>66</sup> and as one possibility we propose that the formed  $[\text{Cr}_2\text{C}_6\text{H}_4\text{O}]^+$  ion exhibits the benzo-metallaoxetane structure **15** (Scheme 11); this would be in keeping with the experimental findings that (i) in the secondary reaction of  $[\text{Cr}_2\text{C}_6\text{H}_4\text{O}]^+$  with benzene, clustering to  $[\text{Cr}_2\text{C}_{12}\text{H}_{10}\text{O}]^+$  is observed while ligand-exchange does not occur, and (ii) a slow addition of background water leads to  $[\text{Cr}_2\text{C}_6\text{H}_6\text{O}_2]^+$  which subsequently forms an adduct  $[\text{Cr}_2\text{C}_{12}\text{H}_{12}\text{O}_2]^+$  with benzene instead of exchanging the water ligand for benzene.

Concluding this section, we state that thermalized  $\text{OCrO}^+$  is capable to activate hydrocarbons, including methane and benzene, with moderate to large efficiencies. Three aspects of the rich chemistry of  $\text{OCrO}^+$  should be pointed out.<sup>67</sup> At first, thermochemical arguments imply that changes in multiplicity take place during the oxidation reactions. Secondly,  $\text{OCrO}^+$



**Figure 3.** Calculated potential-energy surface for  $[\text{Cr}_2\text{O}_2]^+$  at the CASPT2D/BS-II/LSD/DZP level of theory. The exit channels leading to  $\text{CrO}^+ + \text{O}$  ( ${}^4\Pi/{}^6\Sigma^+$  and  ${}^6\Pi/{}^6\Sigma^+$ ) +  $\text{O}$  ( ${}^3P$ ) and to  $\text{Cr}^+ + \text{O}_2$  ( ${}^6S$ ) +  $\text{O}_2$  ( ${}^1\Delta_g$ ) were taken from refs 33, 35b, and 37. Crosses denote excitation energies calculated using CASPT2D/BS-I for the various states at the LSD-geometries of the corresponding ground states.

exhibits a clear preference for C–H versus C–C bond activation; the latter is in fact only observed for alkenes. Finally, the product distributions indicate that the activation of hydrocarbons by the dioxide  $\text{OCrO}^+$  involve a single oxo-ligand in the initial step ( $[2 + 2]$  pathway), similar to the reactions of metal monoxides, while there is no direct evidence for a simultaneous addition of the substrate to both oxygen atoms in terms of a  $[3 + 2]$  cycloaddition.

**Dissociation of  $[\text{Cr}_2\text{O}_2]^+$  and Chromium-Mediated Activation of Dioxygen.** In this section we address the dissociation of  $\text{OCrO}^+$  ( ${}^2A_1$ ) into the ground-state asymptote  $\text{Cr}^+ + \text{O}_2$  ( ${}^3\Sigma_g^-$ ) and vice versa, i.e., the formation of chromium dioxide from this entrance channel via bond activation of molecular oxygen by  $\text{Cr}^+$ . Let us first consider the theoretical aspects: For either the  ${}^2A_1$  or  ${}^2B_2$  states, dissociation of  $\text{OCrO}^+$  into the ground states  $\text{Cr}^+ + \text{O}_2$  ( ${}^3\Sigma_g^-$ ) is spin-forbidden, and the energetically lowest-lying allowed pathway leads to the formation of excited  $\text{Cr}^+ + \text{O}_2$  ( ${}^4D + \text{O}_2$  ( ${}^3\Sigma_g^-$ )). Nevertheless, spin-orbit coupling (SOC) may render dissociation into the ground states possible via curve crossing. In order to construct a rather qualitative potential-energy surface for the  $[\text{Cr}_2\text{O}_2]^+$  system, we computed several vertical excitations of the ground states of structures **1–3** into different multiplicities (Figure 3). Inspection of the surface reveals that a *direct* activation of  $\text{O}_2$  ( ${}^3\Sigma_g^-$ ) by ground-state  $\text{Cr}^+ + \text{O}_2$  ( ${}^6S$ ) to form  $\text{OCrO}^+$  ( ${}^2A_1$ ) cannot occur at thermal energies, even if spin-orbit coupling (SOC) would be very efficient. This conclusion is based on the following arguments: (i) Even upon reduction of the symmetry group to  $C_s$ , the ground states of the isomers  $\text{OCrO}^+$  and  $\text{Cr}(\text{O}_2)^+$  transform to two different hypersurfaces ( $A_1 \rightarrow A'$  and  $B_2 \rightarrow A''$ , respectively); note, however, that this argument does not

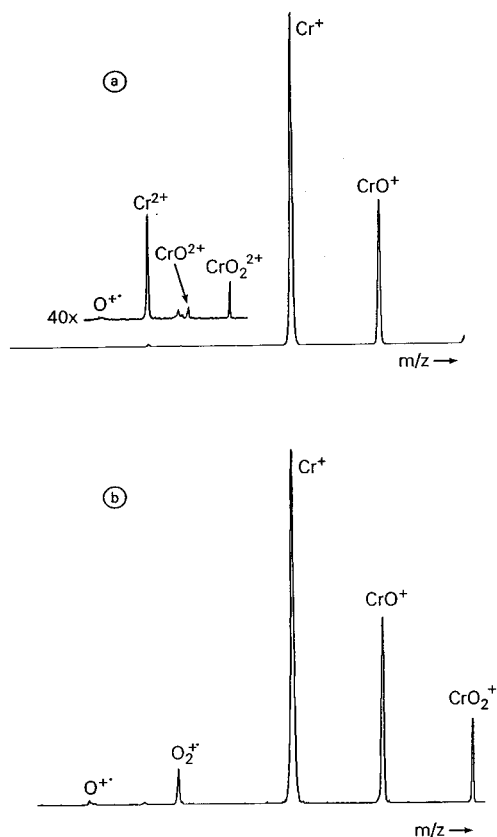
(63) Blumenberg, B. *Nachr. Chem. Techn. Lab.* **1994**, 42, 480.

(64) (a) Stöckigt, D.; Schwarz, H. *Chem. Ber.* **1994**, 127, 2499. (b) Stöckigt, D.; Schwarz, H. *Liebigs Ann.* **1995**, 429.

(65) Becker, H.; Schröder, D.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, 116, 1096.

(66) Schröder, D.; Zummack, W.; Schwarz, H. *Organometallics* **1993**, 12, 1079.

(67)  $\text{OMo}^+$ , the higher homologue of  $\text{OCrO}^+$ , is much less reactive toward hydrocarbons; see: Cassady, C. J.; McElvany, S. W. *Organometallics* **1992**, 11, 2367.



**Figure 4.** (a) CA mass spectrum (O<sub>2</sub>, 80% T) of [Cr,O<sub>2</sub>]<sup>+</sup> obtained by chemical ionization of Cr(CO)<sub>6</sub> with O<sub>2</sub>, (b) NR mass spectrum (Xe 80% T; O<sub>2</sub> 80% T).

apply for <sup>2</sup>B<sub>2</sub> as the ground state of OCrO<sup>+</sup>. (ii) SOC can only occur between surfaces which differ in spin multiplicity by a maximum of two (one spin inversion), such that SOC does not allow for a direct connection of the sextet and doublet surfaces but rather has to involve an intermediate quartet state.<sup>68,69</sup> (iii) The potential intermediate OCrO<sup>+</sup> (<sup>4</sup>A'') is energetically very close to the Cr<sup>+</sup> + O<sub>2</sub> entrance channel, such that even low barriers associated with stepwise SOC from the sextet to the doublet would prevent formation of OCrO<sup>+</sup> (<sup>2</sup>A<sub>1</sub>) from the thermalized reactants. At elevated energies, OCrO<sup>+</sup> (<sup>4</sup>A'') may be formed in a spin-allowed path (Figure 3), but one SOC to the doublet ground state remains.

On the one hand, Figure 3 implies that under thermal conditions a Cr<sup>+</sup>-catalyzed oxidation using molecular oxygen as terminal oxidant cannot be realized in the gas phase. On the other hand, the potential-energy surface leads to the proposal that other states or isomers but doublet OCrO<sup>+</sup> exist and may be generated and characterized experimentally. To this end, we subjected a mixture of Cr(CO)<sub>6</sub> and O<sub>2</sub> to chemical ionization (CI) and recorded the CA and NR mass spectra of the [Cr,O<sub>2</sub>]<sup>+</sup> species formed.<sup>18</sup> Both spectra reveal substantial differences as compared to the corresponding spectra of the OCrO<sup>+</sup> ion generated by EI of CrO<sub>2</sub>Cl<sub>2</sub> (Figure 1). In the CA spectrum (Figure 4a) the ratio CrO<sup>+</sup>:Cr<sup>+</sup> is reversed and amounts to ca.

(68) One reviewer has argued that formal spin-pairing of <sup>6</sup>Cr<sup>+</sup> and <sup>3</sup>O<sub>2</sub> should lead to a quartet state of [Cr,O<sub>2</sub>]<sup>+</sup> without involving curve crossing while formation of <sup>6</sup>Cr(O<sub>2</sub>)<sup>+</sup> should require a spin-flip. Therefore, it seems worthy to clarify that simple spin counting, i.e., Cr<sup>+</sup> (↑↑↑↑) + O<sub>2</sub> (↑↑) → Cr(O<sub>2</sub>)<sup>+</sup> (↑↑↑↑↑) and Cr<sup>+</sup> (↑↑↑↑) + O<sub>2</sub> (↓↓) → Cr(O<sub>2</sub>)<sup>+</sup> (↑↑↑↓↑), is not at all appropriate for the evaluation of spin conservation rules. Rather, the possible spin couplings of two separated fragments must be derived from a vector model (ref 69) using a multireference approach. In fact, it turns out that the process <sup>6</sup>Cr<sup>+</sup> + <sup>3</sup>O<sub>2</sub> → <sup>6</sup>Cr(O<sub>2</sub>)<sup>+</sup> does not require curve crossing.

(69) Herzberg, G. *Molecular Spectra and Molecular Structure*; Krieger, Malabar, 1989; Vol. 1, p 319.

1:2 as compared to ca. 2:1 in Figure 1a. The most notable difference, however, concerns the dication signals in that these are more intense and CrO<sub>2</sub><sup>2+</sup> is much larger for the ion generated by CI of the Cr(CO)<sub>6</sub>/O<sub>2</sub> mixture than for that obtained by EI of CrO<sub>2</sub>Cl<sub>2</sub>. Similarly, in the NR spectrum (Figure 4b) the signals for Cr<sup>+</sup> and O<sub>2</sub><sup>+</sup> are much more abundant than in Figure 1b, while the intensity of CrO<sup>+</sup> decreases. In addition, the recovery signal for OCrO<sup>+</sup> is less intense in Figure 4b, which implies that for this [Cr,O<sub>2</sub>]<sup>+</sup> ion the efficiency of the NR process is smaller as compared to doublet states of OCrO<sup>+</sup>. These differences in intensities suggest that other isomers of [Cr,O<sub>2</sub>]<sup>+</sup> are formed in the CI experiment.

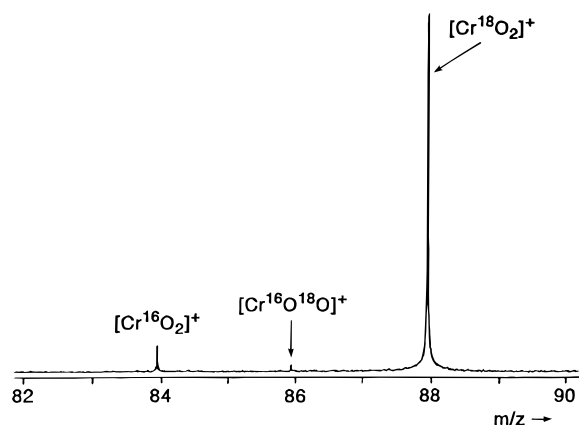
Besides these qualitative aspects, there exists a quantitative difference between the [Cr,O<sub>2</sub>]<sup>+</sup> ions formed by either EI of CrO<sub>2</sub>Cl<sub>2</sub> or CI of Cr(CO)<sub>6</sub>/O<sub>2</sub> with respect to the second ionization energies as expressed in terms of Q<sub>min</sub> values (see experimental details):<sup>21</sup> For the chromium dioxide cation generated from CrO<sub>2</sub>Cl<sub>2</sub> we determined a Q<sub>min</sub> value of 19.2 ± 0.7 eV, while for the ion formed from the Cr(CO)<sub>6</sub>/O<sub>2</sub> mixture, it is significantly lower (Q<sub>min</sub> = 15.7 ± 1.3 eV).<sup>70</sup> This observation proves that at least two different states and/or structures of [Cr,O<sub>2</sub>]<sup>+</sup> were sampled in the charge-stripping experiment, i.e., the ground state OCrO<sup>+</sup> (<sup>2</sup>A<sub>1</sub>) exhibits a high Q<sub>min</sub> to form the corresponding chromium dioxide dication CrO<sub>2</sub><sup>2+</sup>, while the [Cr,O<sub>2</sub>]<sup>+</sup> ion from CI of Cr(CO)<sub>6</sub>/O<sub>2</sub> is either excited by ca. 3.5 eV as compared to OCrO<sup>+</sup> (<sup>2</sup>A<sub>1</sub>) and/or the lower Q<sub>min</sub> is due to the formation of a [Cr,O<sub>2</sub>]<sup>2+</sup> dication with a different structure than that of the dioxide.<sup>71</sup> The latter conjecture is supported by the recent proposal that the dicationic complex Cr<sup>2+</sup>-O<sub>2</sub> can be formed in the reaction of aqueous Cr<sup>2+</sup> with dioxygen.<sup>12</sup>

Although these two [Cr,O<sub>2</sub>]<sup>+</sup> ions were generated under quite different conditions, i.e., EI and CI, the differences in the spectra are not likely to be due to internal energy effects, but rather suggest that different isomers or states of [Cr,O<sub>2</sub>]<sup>+</sup> were formed in both experiments. While for the ion derived from CrO<sub>2</sub>Cl<sub>2</sub> we are quite certain that it corresponds to a doublet state of OCrO<sup>+</sup> (<sup>2</sup>A<sub>1</sub> or <sup>2</sup>B<sub>2</sub>), an assignment for the ion generated from Cr(CO)<sub>6</sub>/O<sub>2</sub> is more difficult: On the one hand, the intense CrO<sup>+</sup> signal upon collisional activation is unexpected for the weakly bound Cr(O<sub>2</sub>)<sup>+</sup> and, further, the observation of a recovery signal in Figure 5b indicates the presence of an inserted structure. On the other hand, the relatively more abundant signals for Cr<sup>+</sup> and O<sub>2</sub><sup>+</sup> in the CA and NR spectra, respectively, point to the presence of the dioxygen complex Cr(O<sub>2</sub>)<sup>+</sup> which may also survive a NR experiment.<sup>14</sup>

One way to clarify this issue is to examine in more detail the formation of [Cr,O<sub>2</sub>]<sup>+</sup> from Cr(CO)<sub>6</sub> and oxygen. Under CI conditions [Cr,O<sub>2</sub>]<sup>+</sup> is likely to be formed in a ligand substitution of Cr(CO)<sup>+</sup> with molecular oxygen. Therefore, we first examined the carbonyl complex [Cr,O<sub>2</sub>•CO]<sup>+</sup> which is formed when a mixture of Cr(CO)<sub>6</sub>, O<sub>2</sub>, and CO (ratio ca. 1:50:50) is subjected to chemical ionization. In principle, these [Cr,O<sub>2</sub>•CO]<sup>+</sup> ions can bear three different connectivities, i.e., (OC)Cr(O<sub>2</sub>)<sup>+</sup>, (OC)Cr(O<sub>2</sub>)<sup>+</sup>, or (O<sub>2</sub>C)CrO<sup>+</sup>. Unimolecular dissociation of the metastable ions (MI) or collisional activation (CA) of [Cr,O<sub>2</sub>•CO]<sup>+</sup> ions leads to four fragmentations (Scheme 12).

(70) The relatively large error in the determination of the Q<sub>min</sub> value is due to a sensitive dependence of the data on ion source conditions rather than too low ion intensities.

(71) Preliminary calculations using the LSD approach and CASPT2D/B3-I demonstrate that bent Cr(O<sub>2</sub>)<sup>2+</sup> (<sup>5</sup>A'') is in fact more stable than CrO<sub>2</sub><sup>2+</sup> (<sup>1</sup>A<sub>1</sub>). In terms of second IEs, this difference translates to 16.1 eV for Cr(O<sub>2</sub>)<sup>2+</sup> versus 17.7 eV for OCrO<sup>+</sup>. However, a more detailed theoretical treatment is indicated: Kretzschmar, I.; Fiedler, A.; Schröder, D.; Schwarz, H., unpublished results.



**Figure 5.** Partial  $^{16}\text{O}/^{18}\text{O}$  exchange in the reaction of  $[\text{Cr},^{18}\text{O}_2]^+$  with  $^{16}\text{O}_2$  (reaction time 5 s,  $p_{\text{O}_2} = 5 \times 10^{-9}$  mbar).  $[\text{Cr},^{18}\text{O}_2]^+$  was generated by reacting mass-selected  $\text{Cr}(\text{CO})^+$  with pulsed-in  $^{18}\text{O}_2$ .

### Scheme 12

		MI	CA
$[\text{Cr},\text{O}_2\cdot\text{CO}]^+$	$\xrightarrow{0.90}$ $[\text{Cr},\text{O}_2]^+ + \text{CO}$	0.60	0.65
	$\xrightarrow{0.02}$ $\text{Cr}(\text{CO})^+ + \text{O}_2$	0.15	0.12
	$\xrightarrow{0.05}$ $\text{CrO}^+ + \text{CO}_2$	0.07	0.08
	$\xrightarrow{0.03}$ $\text{Cr}^+ + \text{CO} + \text{O}_2$	0.18	0.15

The relative abundances for the loss of CO versus  $\text{O}_2$  (Scheme 12) provide evidence against the formation of the dioxygen complex  $\text{Cr}(\text{O}_2)^+$  ( $6A''$ ) from  $[\text{Cr},\text{O}_2\cdot\text{CO}]^+$ , because the large difference of the binding energies of  $\text{O}_2$  and CO to  $\text{Cr}^+$  cation (9.5 kcal/mol versus 21.4 kcal/mol<sup>72</sup>) suggests a reversed ratio for  $(\text{OC})\text{Cr}(\text{O}_2)^+$ ; consequently, the structure  $(\text{OC})\text{Cr}(\text{O}_2)^+$  is implied for the precursor ion and that of  $\text{OCrO}^+$  for the product.<sup>73</sup> For a further characterization of the  $[\text{Cr},\text{O}_2]^+$  ion formed by unimolecular loss of CO from  $[\text{Cr},\text{O}_2\cdot\text{CO}]^+$ , the product ion was subjected to a further collision experiment. In the corresponding MI/CA spectrum, the  $\text{Cr}^+:\text{CrO}^+$  ratio amounts to 1.5:1 which is close to the 2:1 ratio in Figure 4a, but rather different from the 1:2 ratio for the genuine  $\text{OCrO}^+$  species (Figure 1a). Following the arguments concerning the competitive elimination of CO versus  $\text{O}_2$ , a  $\text{Cr}(\text{O}_2)^+$  species cannot be formed, and hence we conclude that another state than  $\text{OCrO}^+$  ( $2A_1$ ) must have been formed in the unimolecular dissociation. In addition, loss of  $\text{CO}_2$  is in line with the formation of  $(\text{OC})\text{Cr}(\text{O}_2)^+$ , but also with  $(\text{O}_2\text{C})\text{CrO}^+$ . However, the relatively large abundance of bare  $\text{Cr}^+$ , even for the metastable ions, is somewhat surprising for  $(\text{OC})\text{Cr}(\text{O}_2)^+$ ; rather, it points to sequential losses of the carbonyl and oxygen ligands from  $(\text{OC})\text{Cr}(\text{O}_2)^+$ . Thus, it seems as if CI of  $\text{Cr}(\text{CO})_6/\text{O}_2$  gives rise to a mixture of different  $[\text{Cr},\text{O}_2]^+$  ions.

The possible formation of other ions than doublet  $\text{OCrO}^+$  was further examined under FTICR conditions by reacting  $[\text{Cr},^{18}\text{O}_2]^+$ , formed from  $\text{Cr}(\text{CO})^+$  and pulsed-in  $^{18}\text{O}_2$  with  $^{16}\text{O}_2$  (Figure 5). The observation of a weak signal for  $[\text{Cr},^{16}\text{O},^{18}\text{O}]^+$  and a more intense one for  $[\text{Cr},^{16}\text{O}_2]^+$  suggest that  $^{16}\text{O}/^{18}\text{O}$  exchange can either occur sequentially or involves the complete oxygen ligand.<sup>74</sup> Further, exchange of the oxygen ligand with background water to yield (unlabeled)  $\text{Cr}(\text{OH}_2)^+$  takes place.

(72) Armentrout, P. B.; Kickel, B. L., In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, 1996, p 1.

(73) This argument is based on the kinetic method; for a review, see: Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1995**, *13*, 287.

(74) The reaction kinetics were complicated and were not resolved, because several processes compete, e.g. dissociation and  $^{16}\text{O}/^{18}\text{O}$ -exchange of  $\text{Cr}(\text{O}_2)^+$  ( $6A''$ ), stepwise isotopic exchange and quenching of  $\text{OCrO}^+$  ( $4A''$ ) to the  $\text{OCrO}^+$  ( $2A_1$ ) ground state; the latter ion is unreactive toward  $\text{O}_2$ .

These findings are in marked contrast to the fact that  $\text{OCrO}^+$  generated by EI of  $\text{CrO}_2\text{Cl}_2$  does hardly undergo any  $^{16}\text{O}/^{18}\text{O}$  exchange with  $^{18}\text{O}_2$  (<1%) and does not react with  $\text{H}_2\text{O}$  except for a slow association to form  $(\text{H}_2\text{O})\text{Cr}(\text{O}_2)^+$ . According to the calculated potential-energy surface (Figure 3), exchange of the  $^{18}\text{O}_2$  ligand by  $^{16}\text{O}_2$  or water point to the formation of the dioxygen complex  $\text{Cr}(\text{O}_2)^+$  ( $6A''$ ), while the occurrence of sequential exchanges of the  $^{18}\text{O}$ -label indicate the presence of a chromium dioxide cation other than  $\text{OCrO}^+$  ( $2A_1$ ). In principle, these findings would offer the possibility to examine state-selective reactions under FTICR conditions, once thermalization of the precursor ions can be warranted. However in practice, thorough thermalization of  $[\text{Cr},\text{O}_2]^+$  generated from  $\text{Cr}(\text{CO})_6/\text{O}_2$  is not only associated with substantial losses of intensity (>90%), but further, these  $[\text{Cr},\text{O}_2]^+$  ions exhibit a similar reactivity toward ethene and propane as compared to  $\text{OCrO}^+$  ( $2A_1$ ), and the only significant difference is a shift of the product distribution toward more energetic products (e.g. more  $\text{Cr}^+$ ). The most intriguing finding is that after even more careful thermalization the  $[\text{Cr},\text{O}_2]^+$  ions generated from  $\text{Cr}(\text{CO})^+$  and  $\text{O}_2$  do not undergo charge transfer with hexafluorobenzene (IE = 9.9 eV). The lowest excited state  $\text{OCrO}^+$  ( $4A''$ ) is ca. 1.5 eV more energetic than  $\text{OCrO}^+$  ( $2A_1$ ) (IE =  $9.7 \pm 0.2$  eV), and both ions can lead to neutral  $\text{CrO}_2$  in its triplet ground state.<sup>14</sup> Therefore, the absence of electron transfer suggests that the fraction of ions (ca. 5%) which survives thermalization in the presence of hexafluorobenzene corresponds to  $\text{OCrO}^+$  in its doublet ground state.

Let us summarize these findings: First, CA and NR spectra demonstrate that CI of  $\text{Cr}(\text{CO})_6/\text{O}_2$  gives rise to different  $[\text{Cr},\text{O}_2]^+$  ions than does EI of  $\text{CrO}_2\text{Cl}_2$ . Secondly, the experiments with the  $[\text{Cr},\text{O}_2\cdot\text{CO}]^+$  complex as well as the  $^{16}\text{O}/^{18}\text{O}$  exchanges of  $[\text{Cr},\text{O}_2]^+$  under FTICR conditions indicate that a mixture of  $^6\text{Cr}(\text{O}_2)^+$ ,  $^4\text{OCrO}^+$ , and  $^2\text{OCrO}^+$  has been generated. However, either in the course of ion/molecule reactions or as a consequence of the thermalizing collisions, this mixture ends up in the ground state ion  $\text{OCrO}^+$  ( $2A_1$ ). Hence, the fascinating perspective to examine reactions of state-selected transition-metal ions other than bare atoms was not pursued further,<sup>75</sup> because under FTICR conditions it would suffer from the pitfall that discrimination between kinetic, rovibronic, and electronic excitation is impossible.

Finally, two different routes for the activation of dioxygen by atomic chromium should be considered. While in the neutral  $[\text{Cr},\text{O}_2]$  system the situation seems to be quite similar to the cation surface,<sup>14</sup> the anion and dication surfaces arise from lower spin states which may help to circumvent the spin-inversion problem, we encounter in the  $[\text{Cr},\text{O}_2]^{+/0}$  systems. Due to the quartet ground state<sup>15b</sup> of  $^4\text{CrO}_2^-$  direct association of  $^5\text{Cr}^-$  anion with  $^3\text{O}_2$  is spin-allowed, but not very promising, because the electron affinity of Cr is low (0.7 eV), such that electron detachment is likely to occur. However,  $[\text{Cr},\text{O}_2]^-$  anions are easily accessible by CI of  $\text{Cr}(\text{CO})_6/\text{O}_2$  in the negative ion mode. Similar to the related  $[\text{Fe},\text{O}_2]^-$  system,<sup>18b,c</sup> the  $^- \text{NR}^+$  spectrum of  $[\text{Cr},\text{O}_2]^-$  is in keeping with an inserted chromium(III) dioxide anion, i.e.:  $\text{OCrO}^+$  (40%),  $\text{CrO}^+$  (100%),  $\text{Cr}^+$  (90%),  $\text{O}_2^{\bullet+}$  (<1%). However, the mechanism for the formation of  $\text{CrO}_2^-$  from this mixture is different from the desired combination of atomic chromium with oxygen, because also oxidations of the carbonyl ligands take place,<sup>15a</sup> e.g.,  $(\text{CO})_n\text{Cr}^- + \text{O}_2 \rightarrow (\text{CO})_{n-1}\text{CrO}^- + \text{CO}_2$ . Another route to chromium dioxide via the dicationic surface has been reported by Bakac and co-workers<sup>12</sup> to play a role in the condensed phase. Under strictly bimolecular collisions in the gas phase, this pathway for dioxide

(75) Review: Armentrout, P. B. *Science* **1991**, *251*, 175.

formation may involve the sequence  ${}^5\text{Cr}^{2+} + {}^3\text{O}_2 \rightarrow {}^5\text{Cr}(\text{O}_2)^{2+} \rightarrow {}^3\text{Cr}(\text{O}_2)^{2+} \rightarrow {}^1\text{CrO}_2^{2+}$ , and the close energy spacing of these states<sup>71</sup> suggests that this route may indeed lead to chromium dioxide. Unfortunately, the intensities of the  $[\text{Cr},\text{O}_2]^{2+}$  dications were too low in our experiments in order to allow for further characterization of the ion as well as an exploration of this attractive perspective.

### Conclusions

Chromium dioxide  $\text{OCrO}^+$  can be generated by electron ionization of chromyl chloride and characterized by collision spectroscopy. According to high-level ab initio calculations  $\text{OCrO}^+$  exhibits two closely spaced doublet ground states ( ${}^2\text{A}_1$  and  ${}^2\text{B}_2$ ), while states of higher multiplicities and the dioxygen complex  $\text{Cr}(\text{O}_2)^+$  are much higher in energy. The high-valent  ${}^2\text{OCrO}^+$  reacts with hydrocarbons including methane and benzene via O-atom transfer from the metal to the substrate. Remarkable is the initial C–H bond activation, which involves a single oxo ligand of the dioxide via a formal [2 + 2] pathway with a different regioselectivity as compared to that of transition-metal monoxide cations.

With respect to catalytic oxidation and the activation of molecular oxygen by  $\text{Cr}^+$ , the computed potential-energy surface

of the  $[\text{Cr},\text{O}_2]^+$  system indicates that the reaction  $\text{Cr}^+ ({}^6\text{S}) + \text{O}_2 ({}^3\Sigma_g^-) \rightleftharpoons \text{Cr}(\text{O}_2)^+ ({}^6\text{A}'') \rightleftharpoons \text{OCrO}^+ ({}^2\text{A}_1)$  is hampered by both spin and symmetry restrictions and cannot occur at thermal energies. This finding accounts for the experimental observation that neither  $\text{Cr}^+$  nor its complexes  $\text{Cr}(\text{L})^+$  with oxidizable ligands L react with dioxygen in the sense of oxidation processes, while  $\text{Fe}^+$  complexes do.<sup>76</sup> Further, a detailed examination of the  $[\text{Cr},\text{O}_2]^+$  system demonstrates that also the more energetic species  ${}^6\text{Cr}(\text{O}_2)^+$  and  ${}^4\text{OCrO}^+$  are experimentally accessible. However, collisional cooling is associated with dissociation and quenching to the ground state  $\text{OCrO}^+ ({}^2\text{A}_1)$ , such that the examination of state-selective reactions of  $[\text{Cr},\text{O}_2]^+$  by means of FTICR technology is not indicated.

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