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## Electron Affinity of Chlorine Dioxide

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maximum activity at optimal  $w_0$  values ranging from 10 to 15. At the same time, adjusting a reversed micellar solution of high  $w_0$  to the optimal range by adding surfactant may not improve catalytic efficiency due to adverse protein-surfactant interactions.<sup>20</sup> The ability to adjust  $w_0$  through hydrate formation (keeping

surfactant concentration constant) may thus have implications to the design of protein-containing reversed micellar systems.

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## Electron Affinity of Chlorine Dioxide

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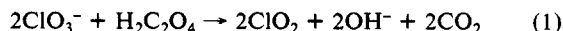
The flowing afterglow technique was used to determine the electron affinity of chlorine dioxide. A value of  $2.37 \pm 0.10$  eV was found by bracketing between the electron affinities of  $\text{HS}^*$  and  $\text{SF}_4$  as a lower limit and that of  $\text{NO}_2$  as an upper limit. This value is in excellent agreement with 2.32 eV predicted from a simple thermodynamic cycle involving the reduction potential of the  $\text{ClO}_2/\text{ClO}_2^-$  couple and a Gibbs hydration energy identical with that of  $\text{SO}_2^*$ .

### Introduction

Recently, the reduction potential of the formate radical,  $\text{CO}_2^*$  was calculated to be  $-1.8$  V from the electron affinity of carbon dioxide and a Gibbs hydration energy estimated to be similar to those of other bent triatomic anions, namely,  $\text{O}_3^*$ ,  $\text{NO}_2^-$ , and  $\text{SO}_2^*$ .<sup>1</sup> The assumption that these anions have similar Gibbs hydration energies can be tested by determining the electron affinity of the chlorine dioxide radical and calculating the Gibbs hydration energy from the difference with the well-known reduction potential of the  $\text{ClO}_{2,\text{ao}}/\text{ClO}_{2,\text{ao}}^-$  couple. In the literature the following values for the electron affinity of chlorine dioxide are found: 2.8 eV,<sup>2</sup> 3.4 eV,<sup>3</sup> 1.8 eV,<sup>4</sup> and a range of 1.3–2.2 eV.<sup>5</sup> If one assumes, given the similarity in molecular parameters,<sup>6</sup> that the Gibbs solvation energy of  $\text{ClO}_2^-$  is similar to that of  $\text{SO}_2^*$ , 134 kJ/mol<sup>1</sup> relative to  $\Delta_f G(H^+) = 0$ , a value of 2.32 eV is predicted from the simple thermodynamic cycle:  $\text{EA} + \Delta_s G^\circ(\text{ClO}_2^-) = E^\circ(\text{ClO}_{2,\text{g}}/\text{ClO}_{2,\text{ao}}^-)$ . The parameters used in this calculation are the reduction potential of  $E^\circ(\text{ClO}_{2,\text{ao}}/\text{ClO}_{2,\text{ao}}^-)$ , 0.934 V at 25 °C,<sup>7,8</sup> and the Gibbs hydration energy of chlorine dioxide,  $-0.4$  kJ/mol.<sup>9</sup> As shown below, a value close to this theoretical estimate is found. An accurate value for the electron affinity of chlorine dioxide might possibly be relevant to reactions of this molecule in the stratosphere. At night chlorine dioxide acts as a reservoir of chlorine monoxide<sup>10</sup> which acts catalytically in the destruction of ozone.<sup>11</sup>

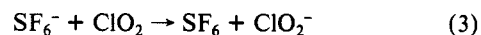
### Experimental Section

Chlorine dioxide was synthesized according to Bray.<sup>12</sup> Briefly, 15 g of oxalic acid and 4 g of potassium chlorate were mixed in a three-neck round-bottom flask that was subsequently kept at 55–60 °C in a water bath. Reaction 1 started after addition of



2 mL of water. Yellow chlorine dioxide gas, free from chlorine, evolved slowly for about 3 h. The presence of carbon dioxide minimizes the risk of an explosion<sup>13</sup> and did not interfere with subsequent reactions. As an additional precaution, the reaction vessel was shielded from direct light by aluminum foil. The employed synthesis is considered safe,<sup>13</sup> and it is therefore unfortunate that the experimental details are not mentioned in a recent monograph on chlorine dioxide.<sup>14</sup> Excess chlorine dioxide was allowed to bubble through a solution of sodium hydroxide solution where it disproportionated.

Experimental determination of the electron affinity of chlorine dioxide was carried out on a flowing afterglow apparatus which has been described in detail elsewhere.<sup>15</sup> The buffer gas employed in all cases was helium which, prior to introduction into the flow tube, was passed through a molecular sieve at 77 K to trap any condensable impurities. All reactions were studied at ambient temperatures at a pressure of 0.3 Torr (40 Pa), corresponding to typical helium flows of on the order of 10 standard liters/min. For charge-exchange reactions involving neutral chlorine dioxide, reactant anions were generated from corresponding neutrals by electron attachment. The  $\text{NO}_2^-$ ,  $\text{SF}_4^-$ ,  $\text{SF}_6^-$ , and  $\text{SO}_2^-$  reactant ions were produced from the corresponding parent neutral molecules, while  $\text{SF}_5^-$ ,  $\text{HS}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  were generated by dissociative electron attachment to  $\text{SF}_6$ ,  $\text{H}_2\text{S}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ , respectively. The  $\text{NO}_3^-$  anion was produced from  $\text{NO}_2$ . These reactant anions were produced upstream near the ion source, and neutral  $\text{ClO}_2$  was introduced approximately 65 cm downstream.  $\text{ClO}_2^-$  was produced upstream via electron transfer from  $\text{SF}_6^-$ :

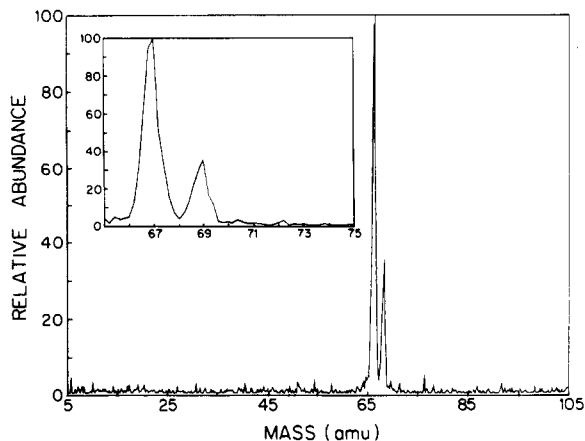


Reaction 2 occurs at approximately the theoretical collision capture

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**Figure 1.** Mass spectrum of  $\text{ClO}_2^-$  reactant ion produced by electron transfer from  $\text{SF}_6^-$  to neutral  $\text{ClO}_2$ . Inset is an expansion of mass region 65–75 showing the locations of  $^{35}\text{ClO}_2^-$  and  $^{37}\text{ClO}_2^-$  at 67 and 69 amu, respectively.

cross section.<sup>16–19</sup> Since the electron affinity of  $\text{SF}_6$  is relatively small, 1.05 eV,<sup>20</sup> reaction 3 is an excellent method for forming reactant anions. The chlorine dioxide flow was adjusted so that  $\text{SF}_6^-$  was depleted in the  $\text{ClO}_2^-$  reactant spectrum. Generation of reactant chlorine dioxide anions in this manner is clean, and only  $\text{ClO}_2^-$  is observed as shown in Figure 1. Reactant neutral gases were added approximately 85 cm downstream of the ion source. Reactant neutral gases as well as source gases for ions other than  $\text{ClO}_2^-$  were obtained commercially and used without purification. For all systems examined, reaction distances were  $\geq 67$  cm, which corresponds to reaction times of at least 15 ms.

## Results

The use of flowing afterglow techniques and ion–molecule charge-transfer reactions to determine electron affinities is presented only briefly since it appears in more detail elsewhere.<sup>21</sup> Because reactions studied in the flowing afterglow apparatus are thermal, observation of the charge-transfer reaction



indicates that  $\text{EA}(\text{C}) \geq \text{EA}(\text{A})$ . If, however, the charge-transfer reaction does not proceed, it is probable that  $\text{EA}(\text{C}) < \text{EA}(\text{A})$ , but caution must be exercised since charge transfer for polyatomic anions does not always occur even when energetically favorable.<sup>22</sup> For this reason, it is best to examine charge-exchange reactions in both directions (that is, to examine both  $\text{A}^- + \text{C}$  and  $\text{C}^- + \text{A}$ ), and we have done so where possible; see Table I. These bracketing experiments place the electron affinity of chlorine dioxide above those for HS and  $\text{SF}_4$  and below that of  $\text{NO}_2$ . From established values for the electron affinities of these species (see Table I), we can place  $\text{EA}(\text{ClO}_2)$  at  $2.37 \pm 0.10$  eV. This value is in excellent agreement with the 2.32 eV predicted from the simple thermodynamic cycle discussed above.

## Discussion

Our charge-exchange reactions indicate that the electron affinity of chlorine dioxide is less than that of nitrogen dioxide but greater

**TABLE I: Charge-Exchange Reactions:  $\text{ClO}_2^- + \text{X}$  and  $\text{X}^- + \text{ClO}_2$**

charge-exchange reaction	EA(X), <sup>a</sup> eV	limit on EA( $\text{ClO}_2$ ), eV
$\text{ClO}_2^- + \text{N}_2\text{O} \rightleftharpoons \text{N}_2\text{O}^-$	$0.2 \pm 0.1$	$\geq 0.2$
$\text{ClO}_2^- + \text{CF}_2\text{Cl}_2 \rightleftharpoons \text{CF}_2\text{Cl}_2^-$	$0.4 \pm 0.2$	$\geq 0.4$
$\text{ClO}_2^- + \text{SF}_6 \rightleftharpoons \text{SF}_6^-$	$1.05 \pm 0.10$	$\geq 1.05$
$\text{SF}_6^- + \text{ClO}_2 \rightarrow \text{ClO}_2^-$	$1.05 \pm 0.10$	$\geq 1.05$
$\text{ClO}_2^- + \text{SO}_2 \rightleftharpoons \text{SO}_2^-$ <sup>b</sup>	$1.107 \pm 0.008$	$\geq 1.107$
$\text{SO}_2^- + \text{ClO}_2 \rightarrow \text{ClO}_2^-$	$1.107 \pm 0.008$	$\geq 1.107$
$\text{ClO}_2^- + \text{CO} \rightleftharpoons \text{CO}^-$	1.4	$\geq 1.4$
$\text{HS}^- + \text{ClO}_2 \rightarrow \text{ClO}_2^-$	$2.32 \pm 0.10$	$\geq 2.32$
$\text{ClO}_2^- + \text{SF}_4 \rightleftharpoons \text{SF}_4^-$ <sup>b</sup>	$2.35 \pm 0.10^c$	$\geq 2.35$
$\text{SF}_4^- + \text{ClO}_2 \rightarrow \text{ClO}_2^-$	$2.35 \pm 0.10$	$\geq 2.35$
$\text{ClO}_2^- + \text{NO}_2 \rightarrow \text{NO}_2^-$	$2.38 \pm 0.06^d$	$< 2.38$
$\text{NO}_2^- + \text{ClO}_2 \rightleftharpoons \text{ClO}_2^-$ <sup>b</sup>	$2.38 \pm 0.06^d$	$< 2.38$
$\text{ClO}_2^- + \text{Cl}_2 \rightarrow \text{Cl}_2^-$	$2.4 \pm 0.2$	$< 2.4$
$\text{SF}_3^- + \text{ClO}_2 \rightleftharpoons \text{ClO}_2^-$	$3.0 \pm 0.3$	$< 3.0$
$\text{I}^- + \text{ClO}_2 \rightleftharpoons \text{ClO}_2^-$ <sup>b</sup>	3.059	$< 3.059$
$\text{Br}^- + \text{ClO}_2 \rightleftharpoons \text{ClO}_2^-$ <sup>b</sup>	3.365	$< 3.365$
$\text{Cl}^- + \text{ClO}_2 \rightleftharpoons \text{ClO}_2^-$	3.617	$< 3.617$
$\text{NO}_3^- + \text{ClO}_2 \rightleftharpoons \text{ClO}_2^-$	$3.9 \pm 0.2$	$< 3.9$

<sup>a</sup> See ref 20. <sup>b</sup> Other bimolecular product channels are present. <sup>c</sup> See ref 5. <sup>d</sup> See ref 21.

than those of HS and  $\text{SF}_4$ . This ordering of electron affinities supports previous work by Dunkin et al.<sup>23</sup> who found that  $\text{EA}(\text{Cl}_2) > \text{EA}(\text{NO}_2) > \text{EA}(\text{HS})$  and determined a value of  $2.38 \pm 0.06$  eV for  $\text{EA}(\text{NO}_2)$ . It is also consistent with our previous work<sup>21</sup> on  $\text{SF}_4$  where charge-transfer reactions indicated the relative order  $\text{EA}(\text{Cl}_2) > \text{EA}(\text{NO}_2) > \text{EA}(\text{SF}_4) > \text{EA}(\text{HS})$ . The compilation by Lias et al.<sup>20</sup> gives a “best” value of 2.30 eV for  $\text{EA}(\text{NO}_2)$ , which along with “best” values for HS and  $\text{SF}_4$  gives the relative ordering  $\text{EA}(\text{SF}_4) > \text{EA}(\text{HS}) > \text{EA}(\text{NO}_2)$ . This is not consistent with our previous  $\text{SF}_4$  work<sup>21</sup> or the work of Dunkin et al.,<sup>23</sup> which place  $\text{EA}(\text{NO}_2)$  above  $\text{EA}(\text{HS})$  and  $\text{EA}(\text{SF}_4)$ . We have chosen, therefore, to use the value 2.38 eV of Dunkin et al.<sup>23</sup> in determining  $\text{EA}(\text{ClO}_2)$  and suggest that this higher value is closer to a “best value” than is 2.30 eV. It is interesting that the average value calculated from all electron affinities in the compilation<sup>20</sup> is 2.39 eV. However, as Table I illustrates, the electron affinities of the group HS,  $\text{SF}_4$ ,  $\text{ClO}_2$ ,  $\text{NO}_2$ , and  $\text{Cl}_2$  are quite similar, and all of the values in fact lie within experimental error of each other. While assignment of more exact electron affinities for these species will require more work, it seems that the relative order  $\text{EA}(\text{Cl}_2) > \text{EA}(\text{NO}_2) > \text{EA}(\text{SF}_4) > \text{EA}(\text{HS})$  is appropriate.

In 1947, Weiss<sup>2</sup> calculated that the sum of the electron affinity and the Gibbs hydration energy of  $\text{ClO}_2^-$  was  $-121.2$  kcal. Estimating the absolute Gibbs hydration energy of chlorine dioxide at  $-55$  kcal/mol, he arrived at the widely quoted value of 2.8 eV. If one repeats his thermodynamic cycle with more recent parameters,<sup>9</sup> a sum of  $-127.2$  kcal results. With the Gibbs hydration energy given above,  $-70.5$  kcal/mol relative to  $\Delta_f G^\circ(\text{H}^+) = 102.5$  kcal/mol,<sup>24</sup> one finds an electron affinity of 2.47 eV, in good agreement with the experimentally determined value.

Wecker et al.<sup>5</sup> have examined the rate coefficients and activation energy for thermal electron capture by chlorine dioxide and deduced a value of  $\text{EA}(\text{ClO}_2) \leq 2.2$  eV. This is based upon a thermodynamic cycle that requires that  $\text{EA}(\text{ClO}_2) < \text{EA}(\text{ClO})$ . Again, our results are in good agreement with this deduced value when one considers that  $\text{EA}(\text{ClO})$  is determined only to about 0.3 eV.

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