assisted substitution owing to the vacancy in its $t_{2g}$ orbitals.[18]

The formation of free $O_2^-/HO_2$ and V(III) appears unlikely. A preliminary investigation of the reaction between V(III) and $HO_2$ generated by pulse radiolysis indicated that $HO_2$ oxidizes V(III) to $VO^{2+}$ with a second-order rate constant $k(\text{V(III)} + HO_2) = 6 \times 10^3\ M^{-1}\ s^{-1}$ in 0.12 M $HClO_4$. Although this rate constant increases with lowered $[H^+]$, the formation of major amounts of $VO^{2+}$ in the $V^{2+}/O_2$ system would require that $HO_2$ react very slowly with $V^{2+}$, especially under those conditions where $[V^{2+}]_0$ is in large excess. This and the general kinetic complexity of the system cause us to exclude a mechanism based on simple outer-sphere electron transfer.

Reactions between $V^{2+}$ and halogens ($X_2$; X = Cl, Br, I) occur at rates similar to that of reaction 3, $V^{3+}$ however being the only product.[10] The difference in basicity of the half-reduced intermediates ($pK_{HO_2} = 4.8 \gg pK_{X_2H}$)[19] in the two systems (ligand basicity is a factor in the rates of $V^{3+}$ substitution reactions)[20] may account for the difference in products if dissociation of a $V^{3+}/X_2^-$ successor complex is much more rapid than ligand substitution.

## Conclusion

The reaction between $V^{2+}$ and molecular oxygen proceeds by parallel pathways, resulting in a [V(II)]-dependent stoichiometry. At low [V(II)] (<0.005 M) one molecule of $VO^{2+}$ is produced per molecule of $O_2$ consumed. At [V(II)] > 0.1 M, no free peroxide is formed and two vanadyl ions $VO^{2+}$ are the immediate reaction products. This is explained by a mechanism involving a [V(II)]-dependent equilibrium between a mononuclear Vanadium(IV) peroxide and a dinuclear vanadium(III) peroxide intermediate.

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# Evidence from the Reaction between Trioxodinitrate(II) and $^{15}NO$ That Trioxodinitrate(II) Decomposes into Nitrosyl Hydride and Nitrite in Neutral Aqueous Solution

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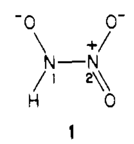
An attempt was made to trap nitrosyl hydride (nitroxyl; HNO, $NO^-$ at pH 7) with $^{15}NO$ in order to decide whether trioxodinitrate(II) (Angeli's salt; oxyhyponitrite; $Na_2N_2O_3$, $HN_2O_3^-$ at pH 7) decomposes in neutral aqueous solution into nitroxyl plus nitrite or into NO plus $HONO^-$ as intermediate products. Final products are $N_2O$ and nitrite. The reaction of $^{15}NO$ with nitroxyl was expected to double the yields of both $N_2O$ and nitrite relative to those normally produced from trioxodinitrate alone and also to provide $N_2O$ with a particular isotopic signature. The yields of $N_2O$ and nitrite and the isotope distributions in product $N_2O$ and the $^{15}NO$ pool strongly support the view that trioxodinitrate decomposes into nitroxyl and nitrite. In the trapping of nitroxyl by $^{15}NO$, little exchange of $^{15}NO$ and $^{14}NO^-$ was observed. In addition to the trapping reaction, a fraction of the nitroxyl can partition by dimerization/dehydration to form $^{14}N_2O$. On the basis of these data and certain rate constants from the literature, a rate constant between $1.8 \times 10^9$ and $7.2 \times 10^9\ M^{-1}\ s^{-1}$ is estimated for the dimerization/dehydration of nitroxyl at pH 7.0, 25 °C. The reaction is thus diffusion-controlled or nearly so. The calculation leading to the above rate constant is not free from kinetic ambiguity, but ambiguity could be largely removed if $N_2O_2^-$, a presumed intermediate in the trapping reaction, were asymmetrical.

## Introduction


1

There is some question[1] as to whether trioxodinitrate(II) ($Na_2N_2O_3$; Angeli's salt;[2] oxyhyponitrite[3]) decomposes to yield as intermediate products nitrosyl hydride ($HNO/NO^-$; nitroxyl) from N(1) of **1** and nitrite from N(2) in neutral aqueous solutions[4-9] (eq 1–3) or, alternatively, NO from N(1) and $HONO^-$ from N(2)[1] (eq 4–8). At pH 7, the monoanion, **1**, is the principal

$$\mathbf{1} \xrightarrow{\text{rds}} NO^- + NO_2^- + H^+ \qquad pK \text{ of HNO} = 4.7\text{[12]} \tag{1}$$

$$NO^- + H^+ \rightarrow {}^1/_2 N_2O + {}^1/_2 H_2O \tag{2}$$

$$\text{net:}\quad \mathbf{1} \rightarrow {}^1/_2 N_2O + NO_2^- + {}^1/_2 H_2O \tag{3}$$

$$\mathbf{1} \xrightarrow{\text{rds}} NO + HONO^- \tag{4}$$

$$\mathbf{1} + HONO^- \rightarrow \mathbf{1}^- + NO_2^- + H^+ \tag{5}$$

$$\mathbf{1}^- + NO \rightarrow [ONNOHNO_2]^{2-} \tag{6}$$

$$[ONNOHNO_2]^{2-} \rightarrow N_2O + NO_2^- + OH^- \tag{7}$$

$$\text{net:}\quad 2\,\mathbf{1} \rightarrow N_2O + 2NO_2^- + H_2O \tag{8}$$

form in aqueous solution[10] ($pK_1 = 2.5$; $pK_2 = 9.7$[11]). Although nitroxyl is not involved in eq 4–8, $N_2O$ must nevertheless arise from N(1). Thus, in the putative intermediate, $[ONNOHNO_2]^{2-}$,

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**Table I.** Products of Decomposition of the Trioxodinitrate Monoanion at pH 7.0, 25 °C, under Anaerobic Conditions in the Presence and Absence of $^{15}NO$ (nmol of N)

| system | $^{14}NO$ | $^{15}NO$ | $^{14}N_2O$ | $^{14,15}(N_2)O$ | $^{15}N_2O$ | total $NO_2^-$ | total $NO_3^-$ |
|---|---|---|---|---|---|---|---|
| complete[a] | 290 | 11 080 | 190 | 1840 | 450 | 2530[b] | ≤70 |
| complete[a] | 320 | 11 210 | 170 | 2150 | 530 | 2820[b] | ≤70 |
| minus $^{15}NO$ | 15 | ≤5 | 1190 | ≤5 | ≤5 | 1200 | ≤70 |
| minus $HN_2O_3^-$ | 140 | 13 700 | ≤5 | ≤5 | 7 | 490 | ≤70 |

[a] The complete reaction mixture contained 13.7 μmol of $^{15}NO$ (~73 μM) and 1.2 μmol of $HN_2O_3^-$ in 1 mL of 50 mM potassium phosphate buffer, pH 7.0. [b] Corrected for $NO_2^-$ arising from $O_2$ contamination[14] by subtracting the amount of $NO_2^-$ formed in vial designated "minus $HN_2O_3^-$".

the N atoms must arise from N(1), N(1), and N(2), from left to right.

Evidence favoring the nitroxyl pathway (eq 1–3) includes the inhibition of decomposition by nitrite[4] (presumably by reversal of the heterolytic bond cleavage of eq 1), the apparent trapping of a monomeric $N^+$ species by $NH_2OH$,[5] tetracyanonickelate(II),[6] or methemoglobin or -myoglobin,[9] and the cross-dimerization/dehydration of nitroxyl produced simultaneously by decomposition of **1** with nitroxyl produced by other reactions.[7,8] Evidence for the NO pathway (eq 4–8) comes from the reaction of **1** with hemoglobin, some results of which are now questioned.[13]

A likely distinction between the nitroxyl and NO pathways could be made by allowing **1** to decompose in the presence of $^{15}NO$, which can trap nitroxyl.[12] Grätzel et al.[12] report that $NO^-$, formed from NO in neutral aqueous solution by pulse radiolysis, reacts rapidly and sequentially with NO to form $N_3O_3^-$, which decomposes rapidly into $N_2O$ and nitrite (eq 9–12).

$$NO^- + NO \rightarrow N_2O_2^- \qquad (9)$$

$$k_9 = 1.7 \times 10^9\ M^{-1}\ s^{-1} \qquad K_9 = 3.5 \times 10^{-5}\ M$$

$$pK \text{ of } HN_2O_2 = 3.5^{12}$$

$$N_2O_2^- + NO \rightarrow N_3O_3^- \qquad (10)$$

$$k_{10} = 4.9 \times 10^6\ M^{-1}\ s^{-1} \qquad pK \text{ of } HN_3O_3 = 3.1^{12}$$

$$N_3O_3^- \rightarrow N_2O + NO_2^- \qquad (11)$$

$$k_{11} = 87\ s^{-1\,12}$$

$$\text{net:}\quad NO^- + 2NO \rightarrow N_2O + NO_2^- \qquad (12)$$

It is assumed in the following predictions that $N_2O_2^-$ and $N_3O_3^-$ are noncyclic and symmetrical intermediates. If **1** were to decompose in excess $^{15}NO$ (e.g. $^{15}NO$/**1** mole ratio = 10–20) and if nitroxyl trapping were 100% effective (only eq 1 and 9–12 apply), then (a) the yields of $N_2O$ and nitrite should be twice those expected for decomposition of **1** alone, (b) there should be little or no $^{14}N_2O$ produced, (c) the $^{14,15}(N_2)O/^{15}N_2O$ mole ratio should be 3, (d) the atomic fractions of $^{14}N$ and $^{15}N$ in $N_2O$ should be 0.38 and 0.62, respectively, and (e) little $^{14}NO$ should enter the $^{15}NO$ pool if $NO/NO^-$ electron exchange were slow and if eq 9 were effectively irreversible. If $NO/NO^-$ electron exchange were rapid or eq 9 freely reversible, predictions a and b above should apply, but the $N_2O$ produced should be almost exclusvely $^{15}N_2O$ and nearly all of the N(1) $^{14}N$ of **1** should appear in the $^{15}NO$ pool. On the other hand, if eq 5–8 applied, then (a) the yield of $N_2O$ and nitrite should be the same as that expected for **1** alone, (b) half of the N(1) $^{14}N$ of **1** should appear in the $^{15}NO$ pool, and (c) $N_2O$ produced should be almost exclusively $^{14,15}(N_2)O$. $NO/NO^-$ electron exchange would not be relevant to this pathway. In either case, an $NO/NO_2^-$ electron-exchange reaction is too slow at pH 7.0 in the absence of $NO_2$ to be significant.[14]

We now report the results of studies in which **1** decomposes in the presence of excess $^{15}NO$.

## Experimental Section

**Materials.** Sodium trioxodinitrate ($Na_2N_2O_3$) was prepared from butyl nitrate and hydroxylamine in anhydrous methanol/sodium methoxide by the method of Hunt et al.[15] The purity, storage, and prepartion of stock solutions of the salt have been described.[9] $[^{15}N]NaNO_2$ (99 atom %), with a chemical purity of >95% by colorimetric assay, was obtained from Stohler Isotope Chemical Co. (Waltham, MA). Its $^{15}N$ isotope abundance was confirmed.[16] $^{15}NO$ was prepared from $[^{15}N]NaNO_2$ by the method of Schenk[17] except that 100 μL of degassed $H_2O$ (per 10-mL expected yield of NO) was injected into vials containing the dry $FeSO_4$–NaBr–$NaNO_2$ mixture under argon in order to initiate the reaction. $^{15}NO$ formed by this procedure contained <0.04 mol % $N_2O$. Commercial NO (Matheson) was passed through a column of NaOH pellets to remove $NO_2$. NO was transferred to reaction vessels by means of gas-tight syringes previously purged with argon.

**Spectrophotometry.** Reactions were carried out anaerobically in 50 mM potassium phosphate buffer, pH 7.0, at 25 °C under argon or nitric oxide as previously described.[9] The decomposition of **1** was monitored by the decrease in absorbance at 237 nm.[18]

**Gas Chromatography/Mass Spectrometry.** Reactions were carried out in 9-mL vials containing 1 mL of solution under conditions described above, except that the bulk gas was helium. The solutions were vigorously stirred by means of small magnetic stirring bars in order to equilibrate liquid and gas phases rapidly. The amount and isotopic content of NO and $N_2O$ in the gas phase of the reaction vessels were determined by means of a Hewlett-Packard 5992A GC/MS equipped with a Porapak Q column (2.4 m × 3.2 mm) operating at 40 °C.[19] Gas samples of 0.15-mL volume were removed from the vial and expanded into a GC sample loop as previously described.[16] Absolute amounts of NO and $N_2O$ were determined with reference to external standards. Total amounts of gaseous products were calculated from published values of aqueous solubility coefficients[20] and Henry's law.

**Nitrate and Nitrite Analysis.** NO was removed from reaction vessels by repeated evacuation and backfilling with argon prior to analyses. Nitrate was determined colorimetrically by the chromotropic acid method[21] after having destroyed nitrite with sulfamic acid (0.05 g/10 mL of sample).[22] Nitrite was determined colorimetrically by diazotization.[23]

## Results

The first-order rate constant for decomposition of **1** in anaerobic 50 mM potassium phosphate buffer, pH 7.0, 25 °C, was estimated spectrophotometrically for these studies to be $(6.7 \pm 0.7) \times 10^{-4}\ s^{-1}$ (six determinations, [**1**] = 50–100 μM); the previous estimate in this laboratory was $(6.6 \pm 0.4) \times 10^{-4}\ s^{-1}$,[9] and the literature value is taken to be $6.9 \times 10^{-4}\ s^{-1}$.[24] When decomposition of **1** occurred as above in the presence of NO (1 atm = 1.9 mM[20]), a rate constant of $(7.4 \pm 0.7) \times 10^{-4}\ s^{-1}$ was obtained (four determinations, [**1**] = 50–200 μM). At 50–100 μM NO, which was representative of experiments using $^{15}NO$, reaction rates were indistinguishable from those in identical systems lacking NO. We conclude from the above that the decomposition of **1** either is zero

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**Table II.** Products of Decomposition of the Trioxodinitrate Monoanion at pH 7.0, 25 °C, under Anaerobic Conditions in the Presence and Absence of $^{15}NO_2^-$ (nmol of N)

| system | $^{14}NO$ | $^{15}NO$ | $^{14}N_2O$ | $^{14,15}(N_2)O$ | $^{15}N_2O$ | total $NO_2^-$ | total $NO_3^-$ |
|---|---|---|---|---|---|---|---|
| complete[a] | 4 | 2 | 440 | 84 | ≤1 | 2610 | ≤70 |
| minus $^{15}NO_2^-$ | 16 | ≤1 | 580 | ≤1 | ≤1 | 600 | ≤70 |
| minus $HN_2O_3^-$ | ≤1 | 1 | ≤1 | ≤1 | ≤1 | 1900 | ≤70 |

[a] The complete reaction mixture contained 0.6 μmol $HN_2O_3^-$ and 2 μmol $^{15}NO_2^-$ in 1 mL of 50 mM potassium phosphate buffer, pH 7.0.

order in [NO] or involves a major zero-order term and a small presumably first-order term. In any case, the zero-order term clearly predominates under conditions of the $^{15}NO$ experiments (Table I).

Product analysis following reaction of **1** with $^{15}NO$ (Table I) shows that the total amounts of $N_2O$ and nitrite formed are about twice those for **1** alone. $^{14,15}(N_2)O$ is the major gaseous product, and the $^{14,15}(N_2)O/^{15}N_2O$ ratio is about 4. The ratio ranged from 3 to 4 in other experiments. $^{14}N_2O$ was a minor product at 1.2 mM **1** and was virtually undetected at 0.6 mM (data not shown). The atomic fractions of $^{14}N$ and $^{15}N$ in $N_2O$ were 0.44 and 0.56, respectively, if $^{14}N_2O$ was included and 0.40 and 0.60 if it was excluded. Only small amounts of $^{14}NO$ were found in the $^{15}NO$ pool following decomposition of **1**. The actual increase in $^{14}N$ enrichment of the $^{15}NO$ pool in Table I (1.2 atom % relative to the initial amount of $^{15}NO$) is equivalent to 13% of the N(1) of **1**. Nitrate was not detected in any experiment. Essentially all of the nitrogen originally present in NO and **1** at the outset can be accounted for by NO, $N_2O$, and nitrite at the end.

The inclusion of 13 mM dimethyl sulfoxide in reaction systems led neither to methane production nor to significantly different product and isotope distributions. This observation suggests that hydroxyl or other highly reactive radicals are probably not involved in the reaction between **1** and NO.[25,26]

Product analysis following decomposition of **1** in the presence of [$^{15}N$]nitrite (Table II) demonstrates that a little $^{15}N$ appears in product $N_2O$ but is consistent with the finding of Bonner and Ravid[18] that $N_2O$ arises largely from N(1) of **1**. Because nitrite can exchange with N(2) of **1**[4,8,27] and since acetate buffer and perhaps also nitrite can apparently catalyze the interchange of N(1) and N(2),[18,27] it is likely that analogous processes were responsible in Table II for the appearance in $N_2O$ of small amounts of $^{15}N$ from nitrite. The $^{15}N$ observed in $N_2O$ ranged from 8 to 16 atom %. In these experiments we observed, in confirmation of the results of Hughes and Wimbledon,[4] that 2 mM nitrite will significantly inhibit the decomposition of 0.6 mM **1**, particularly toward the end of the reaction.

## Discussion

The results follow closely those predicted for decomposition of **1** by the nitroxyl trapping pathway (eq 1 and 9–12) under conditions where $NO/NO^-$ electron exchange is negligible and eq 9 is effectively irreversible. The results are quite different from those predicted by the NO pathway (eq 4–8). We conclude that **1** decomposes largely or entirely by eq 1 and not eq 4 at pH 7.0.

The formation of some $^{14}N_2O$, when none was expected from eq 1 and 9–12 or from eq 4–8, suggests that dimerization/dehydration of nitroxyl can occur (eq 2) as a minor reaction. Thus nitroxyl trapping is not completely efficient, and as expected, the yield of $^{14}N_2O$ decreased as the $^{15}NO/\mathbf{1}$ mole ratio increased. We estimate from Table I that the nitroxyl produced in eq 1 partitions 0.16[28] into eq 2 and 0.84[28] into eq 9–11 under the conditions of Table I. A second indication that $^{14}N_2O$ arises from dimerization/dehydration of nitroxyl comes from the fact that the observed $^{14}N$ and $^{15}N$ atomic fractions in $N_2O$, excluding $^{14}N_2O$, are similar to those predicted for eq 1 and 9–12.

Good agreement between predictions and observation notwithstanding, there are kinetic ambiguities for which we currently lack satisfactory explanations. Equation 9 was expected to be readily reversible,[12] but yet little exchange occurred between $^{14}NO^-$ and the pool of $^{15}NO$. From the results of Grätzel et al.,[12] $k_{-9}$ should be about 200 times greater than $k_{10}$[NO] when [NO] = 73 μM. Thus, the assumedly symmetrical $N_2O_2^-$ should be able to form and return many times before being converted to $N_3O_3^-$. It is possible that $N_2O_2^-$ is not symmetrical, but the $^{14,15}(N_2)O/^{15}N_2O$ mole ratios observed require at least that $N_3O_3^-$ must be essentially symmetrical.

A second ambiguity concerns calculations to estimate the rate constant, $k_2$, for dimerization/dehydration of nitroxyl. If eq 9 were in fact freely reversible, then eq 10 would be the step that commits nitroxyl to the trapping pathway. The effective rate constant for trapping would be $k_{10}/K_9 = 1.4 \times 10^{11}$ M$^{-2}$ s$^{-1}$, with rate = $(k_{10}/K_9)[^{15}NO]^2[NO^-]$. Early in the reaction of Table I, [$^{15}NO$] ~ 18 μM[28] and rate ~ $5.5 \times 10^{-7}$ M s$^{-1}$ = 0.68[28] × $1.2 \times 10^{-3}$ (M) × $6.7 \times 10^{-4}$ (s$^{-1}$). Thus, [$NO^-$] ~ $1.2 \times 10^{-8}$ M. If the rate term for dimerization/dehydration of nitroxyl were rate = $k_2[NO^-]^2$ ~ $2.6 \times 10^{-7}$ M s$^{-1}$ = 0.32[28] × $1.2 \times 10^{-3}$ (M) × $6.7 \times 10^{-4}$ (s$^{-1}$), then $k_2$ ~ $1.8 \times 10^9$ M$^{-1}$ s$^{-1}$ at 25 °C, pH 7.0. If [$^{15}NO$] were taken to be 37 μM,[28] then $k_2$ ~ $7.2 \times 10^9$ M$^{-1}$ s$^{-1}$. If eq 9 is assumed on the other hand to be irreversible so that eq 9 commits nitroxyl to the trapping pathway, then $k_2$ ~ $8.8 \times 10^{14}$ M$^{-1}$ s$^{-1}$. This is an unreasonably large second-order rate constant in that it exceeds the diffusion-controlled rate constant of about $10^{10}$ M$^{-1}$ s$^{-1}$.[29] Thus, it would appear that eq 9 must be freely reversible to obtain a reasonable value for $k_2$ but must be irreversible to explain the near lack of $NO/NO^-$ exchange. Asymmetry of $N_2O_2^-$ would resolve this ambiguity.

From the above rate constant of $1.8 \times 10^9$ M$^{-1}$ s$^{-1}$ for the dimerization/dehydration of nitroxyl and the data of Table I and Figure 4 of ref 9, we estimate the second-order rate constant for the trapping of nitroxyl by metmyoglobin to be $(6.4 \pm 1.0) \times 10^5$ M$^{-1}$ s$^{-1}$ (error reflecting the data of ref 9). A single analogous rate constant for the trapping of nitroxyl by methemoglobin cannot be calculated because its value depends on the degree of nitrosylation of methemoglobin, probably on account of allosteric interactions. The range of values is from about 3 to $10^5$ to $7 \times 10^5$ M$^{-1}$ s$^{-1}$ for methemoglobin.

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(28) The overall partition fractions for nitroxyl trapping and dimerization/dehydration in Table I are as follows: $f_{\text{trapping}}$ = (nmol of $^{14}N$ in $^{14,15}(N_2)O$)/(nmol of $^{14}N$ in total $N_2O$) = 0.84 (av); $f_{\text{dimerizn}}$ = (nmol of $^{14}N$ in $^{14}N_2O$)/(nmol of $^{14}N$ in total $N_2O$) = 0.16 (av). These fractions represent, of course, the integral over the entire course of decomposition of **1**. Because the trapping reactions (eq 9–11) are assumed to be first order in [$NO^-$] whereas dimerization (eq 2) is assumed to be second order, the initial partition fractions at 1.2 mM **1** can be shown to be 0.68 and 0.32 for trapping and dimerization, respectively. If the initial rate of nitroxyl trapping were $5.5 \times 10^{-7}$ M s$^{-1}$ at 1.2 mM **1** (see text), the initial rate of $^{15}NO$ consumption should be twice this or $1.1 \times 10^{-6}$ M s$^{-1}$. Thus a nominal [$^{15}NO$] of 73 μM would represent only a 1-min buffer against exhaustion of $^{15}NO$ in the aqueous phase. Because the mixing system has a characteristic gas/liquid equilibration time of 0.5–1 min,[14] the actual [$^{15}NO$] at quasi steady state is probably about 37 μM early in the reaction and is unlikely to be less than 18 μM. These values are used for the calculations in the text.

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The rate constant for the dimerization/dehydration of nitroxyl is of interest in biochemistry, because there is reason to believe that denitrifying bacteria may form $N_2O$ by dimerization/dehydration of nitroxyl produced in the reduction of nitrite and/or NO.[8,30]

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**Registry No.** $N_2O_3^{2-}$, 15435-67-3; $NO^-$, 14967-78-3; $^{15}NO$, 15917-77-8.

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# Electrostatic Binding of Bicarbonate and Formate in Viologen-Based Redox Polymers: Importance in Catalytic Reduction of Bicarbonate to Formate

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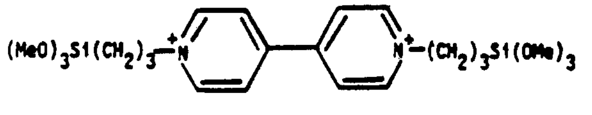
The relative importance of electrostatic binding of $CO_3H^-$ and $HCO_2^-$ in a redox polymer derived from an *N,N'*-dialkyl-4,4'-bipyridinium monomer has been investigated by Fourier transform infrared (FTIR) spectroscopy. At 298 K and a total concentration of C-containing species of 0.1 M the two species are equally firmly bound in a polymer immobilized on a single-crystal Si electrode surface. When the concentration of C-containing species is 1.0 M, the $CO_3H^-$ ion is more firmly bound by about a factor of 2.5, and at a total concentration of 3.0 M the $CO_3H^-$ ion is about 7 times more firmly bound than the $HCO_2^-$ ion. The $HCO_2^-$ and $Cl^-$ anions are equally firmly bound at 1.0 M total anion concentration. On the basis of the lack of change in the cyclic voltammetry response of a derivatized electrode in 1.0 M $Na[CO_3H]$ or $Na[HCO_2]$ compared to 1.0 M NaCl, the exchange rate of the C-containing anions does not appear to be a factor that would limit the rate of reduction of the $CO_3H^-$ ion at an electrode modified with the polymer and impregnated with Pd(0).



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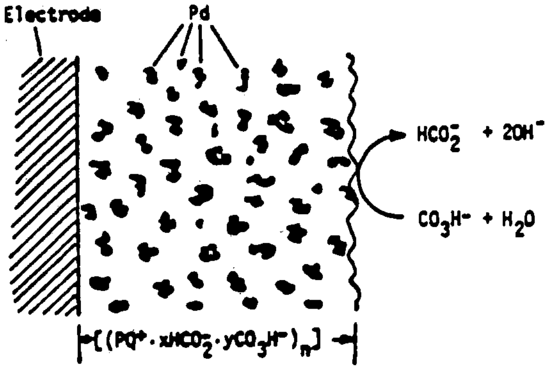
We wish to report results relating to the electrostatic binding of $CO_3H^-$ and $HCO_2^-$ to the polysiloxane polymer derived from the hydrolysis of the viologen derivative represented by I. This work was undertaken with the aim of adding to the characterization of catalytic electrodes for the reduction of $CO_3H^-$ to $HCO_2^-$ (Scheme I).[1-3] It is well-known that ions can be more and less firmly bound into electrode-confined polymers,[4-8] including the $[(PQ^{2+/+})_n]_{surf}$ polymer derived from I.[9] Since the heterogeneous rate constant for the reduction of $CO_3H^-$ at Pd(0) is relatively modest,[2] it is important to be able to take advantage of the three-dimensionality of the polymer/Pd(0) assembly to achieve useful rates of reduction. The point is that there is a potential advantage in terms of efficiency for $HCO_2^-$ formation when Pd(0) and $CO_3H^-$ are concentrated in the redox polymer. Accordingly, the kinetics and thermodynamics associated with binding of the $CO_3H^-/HCO_2^-$ redox reagents and other anions are important in achieving the optimum catalyst system.

Scheme I. Catalytic Electrode for the Reduction of $CO_3H^-$ to $HCO_2^-$ [3]



There is a variety of physical techniques that can be useful in establishing the relative concentration of anionic species bound to a surface-immobilized polymer. In this work we have used Fourier transform infrared (FTIR) spectroscopy to establish the relative importance of the binding of $CO_3H^-$ and $HCO_2^-$ from aqueous solutions of various concentration ratios of these two

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