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Evidence for Adduct Formation between $ONOO^-$ and CO_2 from High-Pressure Pulse Radiolysis

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The activation volume for the reaction of CO_2 with $ONOO^-$ has been determined to be $-22\ cm^3\ mol^{-1}$ using the high-pressure pulse radiolysis technique. The significant negative volume of activation provides conclusive evidence for a short-lived cyclo-adduct formation between $ONOO^-$ and CO_2.

Introduction

Carbon dioxide reacts rapidly with $ONOO^-$, apparently forming an adduct whose composition has been suggested to be $ONOOCO_2^-$.[1] The rate constant for this reaction has been determined to be $3 \times 10^4\ M^{-1}\ s^{-1}$ at 24 °C,[1] and the final products of this reaction were found to be CO_2 and NO_3^-.[2,3] This process has been shown to proceed via the formation of 30−35% $CO_3^{\bullet-}$ and ${}^{\bullet}NO_2$ radicals in the bulk of the solution,[3−5] which in the absence of appropriate scavengers recombine and form CO_2 and NO_3^-.[6,7] Lilie et al.[6] determined the rate constant for the reaction of $CO_3^{\bullet-}$ with ${}^{\bullet}NO_2$ to be $1 \times 10^9\ M^{-1}\ s^{-1}$ using pulse radiolysis, and their findings were consistent with a single kinetic step to yield CO_2 and NO_3^-. Alfassi et al.[7] have recently revised this value to $4.6 \times 10^8\ M^{-1}\ s^{-1}$ and reported that the suggested intermediate was not observed on the microsecond time scale. Furthermore, the reaction of $CO_3^{\bullet-}$ with ${}^{\bullet}NO_2$ does not produce $ONOO^-$ in alkali pH using γ-radiolysis.[7] Thus, the reaction of $CO_3^{\bullet-}$ with ${}^{\bullet}NO_2$ most probably occurs through a N−O coupling to yield the unstable $O_2NOCO_2^-$, which is followed by the rapid cleavage of the O−C bond to produce CO_2 and NO_3^-. In view of the above, the detailed process is presented in Figure 1, where k_3/k_2 has been determined to be about 2.[3−5]

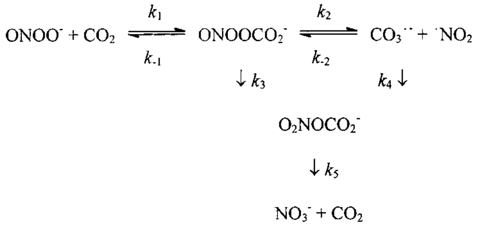

Figure 1. Detailed mechanistic scheme for the reaction of $ONOO^-$ with CO_2.

We report herein that the reaction of CO_2 with $ONOO^-$ is associated with a substantially negative volume of activation of $-22\ cm^3\ mol^{-1}$, which reveals direct evidence for adduct formation between $ONOO^-$ and CO_2.

Experimental Section

Pulse radiolysis was utilized to generate $ONOO^-$ as described previously.[8] The high-pressure setup was described in detail elsewhere.[9] The pressure experiments were performed at 1500 atm and room temperature (18 °C). Briefly, aerated solutions containing 30 mM nitrite, 0.5 M formate, 64−250 mM bicarbonate, and 10 mM Tris buffer (final pH 8.0) were pulse-irradiated. Under these conditions, $O_2^{\bullet-}$ is produced from formate and O_2, and ${}^{\bullet}NO$ from NO_2^-, whereupon ${}^{\bullet}NO$ and $O_2^{\bullet-}$ recombine to yield about 15 μM of $ONOO^-$ in the presence of 64−250 mM bicarbonate. Since ONOOH reacts very slowly with CO_2, if at all,[1] the effect of pressure was studied at pH 8.0, which is sufficiently above the $pK_a(ONOOH) = 6.6$,[1,10] and therefore most of the peroxynitrite is dissociated. Tris buffer was used in order to keep the pH constant since it shows no significant pressure dependence; i.e., the reaction volume associated with the deprotonation of H^+Tris is close to zero.[11,12] The decomposition of $ONOO^-$ was followed at 302 nm.

Results and Discussion

The reaction of ONOO− with excess of CO_2 in aerated solution containing formate was previously shown to yield 30−33% O_2NOO^- using the stopped-flow technique.[5] On the basis of the proposed model (Figure 1, eqs 1−5), the formation of 30−33% $CO_3^{\bullet-}$ and ${}^{\bullet}NO_2$ in the bulk of the solution, followed by the rapid reactions 6−8,[5] can account for this observation, where the reaction of $ONOO^-$ with CO_2 is the rate-determining step for the formation of O_2NOO^-.

$$CO_3^{\bullet-} + HCO_2^- \rightarrow CO_2^{\bullet-} + HCO_3^- \qquad k_6 = 1.6 \times 10^5\ M^{-1}\ s^{-1} \text{ (from ref 6)} \quad (6)$$

$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^{\bullet-} \quad (7)$$

$$O_2^{\bullet-} + {}^{\bullet}NO_2 \rightarrow O_2NOO^- \quad (8)$$

Thus, under these conditions, the absorption at 302 nm decays via two sequential first order reactions. The rate of the first

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TABLE 1: Activation Volume Measured for the Reaction of $ONOO^-$ with CO_2 at pH 8 (10 mM Tris) upon Increasing the Pressure from 1 to 1500 atm

$[HCO_3^-]_o$, mM	$\Delta V^{\ddagger}_{exp}$, $cm^3\ mol^{-1}$	$\Delta V^{\ddagger}(k_o)$, $cm^3\ mol^{-1}$
64	$+5 \pm 2$	-22 ± 3
125	$+1 \pm 3$	-26 ± 4
250	-2 ± 3	-29 ± 4

reaction depends linearly on $[CO_2]$ and is attributed to the formation of O_2NOO^-, which also absorbs at 302 nm. The second slow and pH-dependent reaction is attributed to the decomposition of O_2NOO^- into nitrite and O_2.[5] The same kinetics as described above were observed using pulse radiolysis for the generation of peroxynitrite in the presence of CO_2 and formate in aerated solutions and at pH 8.0. The effect of 1500 atm of pressure on the observed rate constant of the first process was very small, and therefore no measurements were performed between these two extreme points. We always do measure points between only in cases where the pressure effect is indeed larger, as our experience has shown that in the case of such small effects the plots of ln k vs P are always linear. The effect of pressure on the second process was within experimental error the same as that determined previously for the decomposition of O_2NOO^-, i.e., $+6.7 \pm 0.7$ $cm^3\ mol^{-1}$.[13] The results obtained for the first process, namely, for the reaction of $ONOO^-$ with CO_2, are summarized in Table 1.

The concentration of CO_2 at a given pH is determined by equilibrium 9, which is associated with a substantially negative reaction volume, viz., $\Delta V(K_a) = -26$ [14] and -27.0 ± 1.4 [15] $cm^3\ mol^{-1}$.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad K_a \qquad (9)$$

The overall very negative reaction volume implies that the $[CO_2]$ decreases by a factor of about 5 upon increasing the pressure from 1 to 1500 atm, which should lead to a 5-fold decrease in the observed rate constant for the reaction of $ONOO^-$with CO_2. Since no significant decrease in the observed rate constant occurred under pressure (Table 1), we conclude that the process is accelerated by pressure to such an extent that the overall effects approximately cancel. The activation volume for the rate-determining step is given by eq 11, which is based on eq 10.

$$k_{obs} = k_o[CO_2] = k_o[HCO_3^-]_o[H^+]/(K_a + [H^+]) \approx k_o[HCO_3^-]_o[H^+]/K_a \quad (10)$$

$$\Delta V^{\ddagger}_{exp} = \Delta V^{\ddagger}(k_o) - \Delta V(K_a) \quad (11)$$

It follows from the above quoted values for $\Delta V^{\ddagger}_{exp}$ and $\Delta V(K_a)$ that $\Delta V^{\ddagger}(k_o)$ ranges from -22 to -29 $cm^3\ mol^{-1}$, depending on the selected bicarbonate concentration (Table 1). This very negative value for $\Delta V^{\ddagger}(k_o)$ must be due to significant bond formation and/or charge creation in the transition state.

According to the mechanism given in Figure 1, and assuming the steady-state approximation for $ONOOCO_2^-$, rate law 12 is obtained in the presence of 0.5 M formate. Under these conditions $CO_3^{\bullet -}$ is scavenged by formate; i.e., reaction 6 competes efficiently with the recombination of ${}^{\bullet}NO_2$ with $CO_3^{\bullet -}$.

$$-\frac{d[ONOO^-]}{dt} = \frac{k_1(k_2 + k_3)}{k_{-1} + k_2 + k_3}[ONOO^-][CO_2] = k_o[ONOO^-][CO_2] \quad (12)$$

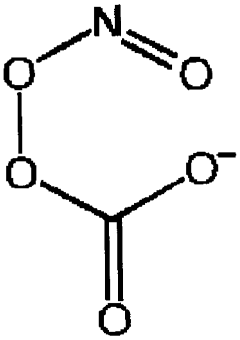

Figure 2. Suggested "cyclic" structure for $ONOOCO_2^-$.

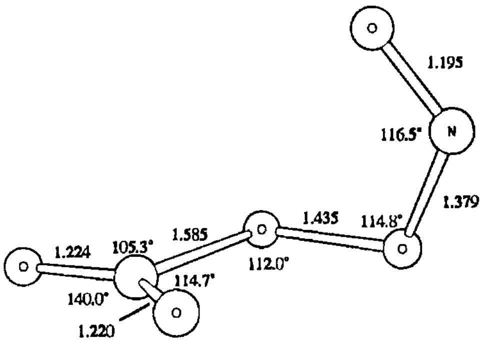

Figure 3. Beckel3LYP/6-31G-optimized structure for $ONOOCO_2^-$. Reprinted with permission from ref 18. Copyright 1996 American Chemical Society.

We now consider two extreme cases for which k_{-1} is much smaller or considerably larger than $(k_2 + k_3)$, where $k_3/k_2 \approx 2$.[3−5]

(i) If k_{-1} is very small, then $k_o \approx k_1$, $\Delta V^{\ddagger}(k_o) \approx \Delta V^{\ddagger}(k_1)$, and k_1 is the rate-determining step. A simple single-bond-formation step is typically characterized by a contribution of -10 $cm^3\ mol^{-1}$ to the observed volume of activation,[16,17] i.e., substantially less negative than that observed in the present case for $\Delta V^{\ddagger}(k_o)$. However, a substantially more negative value of -30 to -35 $cm^3\ mol^{-1}$ would be obtained if bond formation results in a "cyclic" type of reaction product similar to that observed for [4 + 2] cycloaddition reactions.[16,17] In the present case only one bond will be formed, but the predicted structure of the intermediate is such that the orientation of the ONO group is pointing in the direction of $OC(O)O^-$ (Figure 2), and even in the absence of a direct bond formation between these ends of the molecule during rotation in solution, it will sweep out a volume very similar to that for the cyclo-adduct. Thus, the orientation of the free ends of the intermediate may cause a further volume collapse and account for the substantially more negative value for $\Delta V^{\ddagger}(k_o)$.

(ii) If $k_{-1} \gg (k_2 + k_3)$, $k_o \approx K_1(k_2 + k_3)$, and $\Delta V^{\ddagger}(k_o) \approx \Delta V(K_1) + \Delta V^{\ddagger}(k_2 + k_3)$. Houk et al.[18] calculated the optimized structure of $ONOOCO_2^-$ (Figure 3), where the dihedral angle about the O−O bond is 78.9°. This should not significantly affect the volume of the molecule as compared to that of the cyclic structure (Figure 2) when the molecule rotates in solution around the C−O axis formed between C and the remote peroxo oxygen atom. It is therefore reasonable to expect that $\Delta V(K_1)$ will be significantly more negative than $\Delta V^{\ddagger}(k_1)$ since we are moving along the reaction coordinate, where the reaction is complete for $\Delta V(K_1)$ and in a transition state (somewhere along the reaction coordinate) for $\Delta V^{\ddagger}(k_1)$. On the other hand, it is reasonable to expect that $\Delta V^{\ddagger}(k_2 + k_3)$ will be positive and will therefore offset the more negative value expected for $\Delta V(K_1)$. Reaction 2 involves bond breakage, and therefore k_2 is expected to decrease with increasing pressure, i.e., $\Delta V^{\ddagger}(k_2) > 0$. Reaction 3 could either occur intramolecularly, where no major volume increase is expected, or could involve a rate-determining bond breakage followed by a rapid bond formation, which will be associated with a volume increase, i.e., k_3 will decrease with increasing pressure. In the case where k_3 exhibits no meaningful pressure dependence, the contribution of $\Delta V^{\ddagger}(k_2 + k_3)$ will be dominated by the effect of pressure on k_2. In such a case, the effect of pressure on k_o will be reduced to the effect of pressure in the case where $k_o = k_1$, since the activation volumes associated with k_{-1} and k_2 are expected to be very similar since both these reactions involve bond cleavage. Thus, independent of which model applies, the significantly negative volume of activation associated with the overall reaction provides conclusive evidence for adduct formation between $ONOO^-$ and CO_2.

However, in the absence of a radical scavenger and for $k_{-1} \gg (\alpha k_2 + k_3)$, k_o is given by eq 13, where $\alpha = k_4/(k_4 + k_{-2})$.

$$k_o = \frac{k_1(\alpha k_2 + k_3)}{k_{-1} + a k_2 + k_3} = K_1(\alpha k_2 + k_3) = K_1 k_2(\alpha + 2) = 3 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}\ \text{(from ref 1)} \quad (13)$$

Also, the experimental rate constant for the reaction of $^{\bullet}NO_2$ with $CO_3^{\bullet -}$ and the equilibrium rate constant K_1K_2 are given by eqs 14 and 15, respectively.

$$k_{exp} = \left\{k_4 + \frac{k_{-2}(k_{-1} + k_3)}{k_{-1} + \alpha k_2 + k_3}\right\} = (k_4 + k_{-2}) = 4.6 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}\ \text{(from ref 7)} \quad (14)$$

$$K_1K_2 = \frac{[^{\bullet}NO_2]\,[CO_3^{\bullet -}]}{[ONOO^-][CO_2]} = 0.1\ \text{(from ref 19)} \quad (15)$$

From eq 15 it follows that $K_1k_2 = 0.1k_{-2}$, and by inserting this value into eq 13, one calculates that $k_{-2} = (1-1.5) \times 10^5\ \mathrm{M^{-1}\,s^{-1}}$. Thus, k_{-1} can be larger than k_3 provided that $\alpha = 1$; i.e., $k_4/k_{-2} > 4000$. However, Merenyi et al.[10] have recently demonstrated that the reaction of $^{\bullet}OH/O^{\bullet -}$ with $^{\bullet}NO_2$ generates almost equal amounts of $ONOOH/ONOO^-$ and $NO_3^- + H^+$, and we have no reason this should be much different for the reaction of $CO_3^{\bullet -}$ with $^{\bullet}NO_2$; i.e., $k_4/k_{-2} \sim 0.1-10$. Thus, it is most probable that k_{-1} is smaller than k_3, i.e., $k_o = k_1$, and the measured negative volume of activation must therefore be associated with the formation of a cyclo-adduct as discussed above.

One remaining question is the small effect of the bicarbonate concentration on the observed value of $\Delta V^{\ddagger}_{exp}$ (Table 1). An increase in the bicarbonate causes an increase in $[CO_2]$ accompanied by an increase in k_{obs} as expected under pseudo-first-order conditions. This should in principle not affect the value of $\Delta V^{\ddagger}_{exp}$. At higher bicarbonate concentrations, the acid dissociation of bicarbonate and its pressure dependence may interfere with the overall process. The deprotonation of bicarbonate is characterized by a reaction volume of -29.2 cm^3 mol^{-1}.[20] This means that the dissociation of bicarbonate is increased under pressure and could lead to an increase in $[H^+]$, which should be buffered by the Tris buffer. However, at high bicarbonate concentration this may not be the case anymore, and upon increasing the pressure, a small increase in $[H^+]$ may occur, which could cause an increase in $[CO_2]$ coupled to an acceleration of the reaction under pressure. On this basis one could account for the more negative $\Delta V^{\ddagger}_{exp}$ observed at higher bicarbonate concentrations. This would then mean that the lower bicarbonate concentration gives the more accurate data since the Tris buffer is in full control of the process; i.e., $\Delta V^{\ddagger}(k_o) = -22$ cm^3 mol^{-1}. The above outlined argument is also in agreement with the fact that we measured $\Delta V^{\ddagger}_{exp} = -2.7$ cm^3 mol^{-1} in the absence of Tris buffer, i.e., where the dissociation of bicarbonate may control the pH of the solution.

In conclusion, the measured activation volume for the reaction of $ONOO^-$ with CO_2, i.e. -22 cm^3 mol^{-1}, provides conclusive evidence for the formation of an intermediate species in this reaction, and so underlines the validity of the mechanistic conclusions reached on the basis of experimental observations and theoretical predictions.[3-5,7,10,18]

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References and Notes

(1) Lymar, S. V.; Hurst, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 8867.

(2) Uppo, R. M.; Squadrito, G. L.; Pryor, W. A. *Arch. Biochem. Biophys.* **1996**, *327*, 335.

(3) Lymar, S. V.; Hurst, J. K. *Inorg. Chem.* **1998**, *37*, 294.

(4) Goldstein, S.; Czapski, G. *Inorg. Chem.* **1997**, *36*, 5113.

(5) Goldstein, S.; Czapski, G. *J. Am. Chem. Soc.* **1998**, *120*, 3458.

(6) Lilie, J.; Hanrahan, R. J.; Henglein, A. *Radiat. Phys. Chem.* **1978**, *11*, 225.

(7) Alfassi, Z. B.; Dhanasekaran, R. E.; Huie, R. E.; Neta, P. *Radiat. Phys. Chem.* **1999**, *56*, 475.

(8) Goldstein, S.; Czapski, G. *Free Radical Biol. Med.* **1995**, *19*, 505.

(9) Wishart, J. F.; van Eldik, R. *Rev. Sci. Instrum.* **1992**, *63*, 3224.

(10) Merenyi, G.; Lind, J.: Goldstein, S.; Czapski, G. *J. Phys. Chem.* **1999**, *103*, 5685.

(11) Neuman, R. C.; Kauzmann, W.; Zipp, A. *J. Phys. Chem.* **1973**, *77*, 2687.

(12) Kitamura, Y.; Itoh, T. *J. Sol. Chem.* **1987**, *16*, 715.

(13) Goldstein, S.; van Eldik, R.; Meyerstein, D.; Czapski, G. *J. Phys. Chem. A* **1997**, *101*, 7114.

(14) Barbero, J. A.; Hepler, L. G.; McCurdy, K. G.; Tremaine, P. R. *Can. J. Chem.* **1983**, *61*, 2509.

(15) van Eldik, R.; Palmer, D. A. *J. Sol. Chem.* **1982**, *11*, 339.

(16) Klärner, F.-G.; Diedrich, M. K.; Wigger, A. E. In *Chemistry under Extreme or Non-Classical Conditions*; van Eldik, R., Hubbard, C. D., Eds.; Wiley: New York, 1997; Chapter 3.

(17) Drljaca, A.; Hubbard, C. D.; van Eldik, R.; Asano, T.; Basilevsky, M. V.; le Noble, W. J. *Chem. Rev.* **1998**, *98*, 2167.

(18) Houk, K. N.; Condroski, K. B.; Pryor, W. A. *J. Am. Chem. Soc.* **1996**, *118*, 13002.

(19) $\Delta_f G°(ONOO^-) = 16.4$ kcal/mol,[10] $\Delta_f G°(CO_2) = -92.2$ kcal/mol, $\Delta_f G°(CO_3^{\bullet -}) = -89.5$ kcal/mol, and $\Delta_f G°(^{\bullet}NO_2) = 15.1$ kcal/mol. Thus, $\Delta G° = -RT \ln(K_1K_2) = 1.4$ kcal/mol, and $K_1K_2 = 0.1$.

(20) Larson, J. W.; Zeeb, K. G.; Hepler, L. G. *Can. J. Chem.* **1982**, *60*, 2141.