effects, or both inductive and mesomeric origin, in organic chemistry.

Acknowledgment. This work was partially supported by the National Science Foundation under the Contract CHE-9015566 and by the Florida State University through time granted on its VAX and Cray Y-MP digital computers. J.C. also acknowledges support from the Camille and Henry Dreyfus Foundation New Faculty Award Program. The helpful suggestions from Dr. J. P. Ritchie (Los Alamos National Laboratory, Theoretical Division, Group T-14) are appreciated.

Registry No. $(NH_2)_3CCF_3$, 134939-43-8; $(NH_2)_3CC(CN)_3$, 125041-94-3; $(NH_2)_3CC(NO_2)_3$, 125041-93-2.

Chemistry of Large Hydrated Anion Clusters $X^-(H_2O)_n$, $0 \leq n \approx 50$ and X = OH, O, O_2, and O_3. 1. Reaction of CO_2 and Possible Application in Understanding of Enzymatic Reaction Dynamics

X. Yang and A. W. Castleman Jr.*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received February 4, 1991*

Abstract: The reactions of CO_2 with large hydrated anion clusters $X^-(H_2O)_{n=0-59}$, X = OH, O, O_2, and O_3, were studied in a fast-flow reactor under thermal conditions. Interesting solvation effects were found in terms of the observed mechanisms and reaction kinetics. Hydration by only a few water molecules makes O_2^- and O_3^- very inert to attack by CO_2 due to the change in sign of the reaction enthalpy from negative to positive caused by the solvation. In contrast, reactions of hydrated OH^- with CO_2 are exothermic at all degrees of solvation, and the large discrepancy between the experimentally measured rate constants and the theoretically calculated values, also attributable to solvation, can be explained by a consideration of the reaction kinetics in which the unimolecular dissociation rate constant of the reaction intermediate increases and the intermolecular conversion rate constant decreases at progressively larger cluster sizes. An application of this work is found in contributing to a further understanding of the reaction dynamics of enzymatic hydration of CO_2 in biological systems. The present work gives experimental evidence, by bridging the gas and the condensed phase via reactivity studies at different degrees of hydration, to support a proposed mechanism that attributes the enzymatic effect to a decrease in the hydration of OH^- by carbonic anhydrase.

Introduction

There are two prime motivations for studies of clusters: First, the research serves to bridge the gas and condensed phases since, as the degree of the solvation increases, the properties of large gas-phase clusters begin to approach those of the condensed phase.[1] Second, clusters are involved in many research fields like solvation, nucleation, aerosols, and fine particles and in processes such as combustion and catalysis. Investigations of clusters thus offer the promise of contributing to an understanding of these processes at the molecular level.[2] Large hydrated cluster ions are found to play an important role in many atmospheric processes.[3] However, most clusters have been produced and studied to date by using supersonic expansions and other nonthermal techniques,[4] which greatly limits the ability to investigate the properties and determine rates of reactions under well-defined temperatures and pressures. Several research groups have employed fast-flow techniques to study hydrated clusters under thermal conditions,[5] but due to past difficulties in producing large ones, only results with cluster sizes up to $n = 4$ have been reported in the literature for hydrated anionic species.[6]

Employing a flowing afterglow apparatus affixed with a high-pressure ion source, we demonstrated that clusters of $H^+(H_2O)_{n=1-60}$[7] and $X^-(H_2O)_{n=0-59}$ (X = OH, O, O_2, and O_3)[8] could be produced and investigated under well-defined temperatures and pressures. The selection of CO_2 as the reactant neutral in the present work is motivated by the extensive interest in its aqueous chemistry in terms of both environmental and biological sciences. Regarding the first area, there is recognized need for a continuing effort to identify reaction mechanisms of CO_2 that may influence its lifetime in the atmosphere and oceans. Similarly, although it is known that the enzymatic hydrolysis of CO_2 involves its reaction with OH^- in aqueous solution in the presence of enzymes as a catalyst, the basic reaction mechanism and dynamics of reaction of hydrated OH^- with CO_2 has yet to be fully elucidated.[9]

In previous studies, Fehsenfeld and Ferguson[10] determined the rate constants at room temperature for the reactions of CO_2 with various small hydrated anions $OH^-(H_2O)_{n=0-4}$, $O_2^-(H_2O)_{n=0-2}$, and $O_3^-(H_2O)_{n=0-2}$. In a later paper, Fehsenfeld et al.[11] reexa-

---

(1) Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589. Castleman, A. W., Jr.; Keesee, R. G. *Acc. Chem. Res.* **1986**, *19*, 413.

(2) Castleman, A. W., Jr.; Keesee, R. G. *Science* **1988**, *241*, 36.

(3) Ferguson, E. E.; Fehsenfeld, F. C.; Albritton, D. L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, p 45. Arnold, F. In *Atmospheric Chemistry*; Goldberg, E. D., Ed.; Springer-Verlag: Berlin, 1982; p 273. Keesee, R. G.; Castleman, A. W., Jr. *J. Geophys. Res.* **1985**, *90* (D), 5885.

(4) Märk, T. D.; Castleman, A. W., Jr. *Adv. At. Mol. Phys.* **1984**, *20*, 65.

(5) Meot-Ner, M.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 998. Smith, D.; Adams, N. G.; Alge, E. *Planet. Space Sci.* **1981**, *29*, 449. Lau, Y. K.; Ikuta, S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 1462. Viggiano, A. A.; Dale, F.; Paulson, J. F. *J. Chem. Phys.* **1988**, *88*, 2469. Zook, D. R.; Grimsrud, E. P. *J. Phys. Chem.* **1988**, *92*, 6374. Graul, S. T.; Brickhouse, M. D.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 631 and the references therein.

(6) Moruzzi, J. L.; Phelps, A. V. *J. Chem. Phys.* **1966**, *45*, 4617. Golub, S.; Steiner, B. *J. Chem. Phys.* **1968**, *49*, 5191. Ferguson, E. E. *Can. J. Chem.* **1969**, *47*, 1815. Arshadi, M.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1483. Melton, C. E. *J. Phys. Chem.* **1972**, *76*, 3116. Bohme, D. K. In *Ionic Processes in the Gas Phase*; Almoster Ferreira, M. A., Ed.; D. Reidel: Dordrecht, Holland, 1984; p 111. Hierl, P. M.; Ahrens, A. F.; Henchman, M.; Viggiano, A. A.; Paulson, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 3140. Keesee, R. G.; Lee, N.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2599. Thompson, B. A.; Iribarne, J. W. *J. Chem. Phys.* **1979**, *71*, 4451 and references therein.

(7) Yang, X.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6845.

(8) Yang, X.; Castleman, A. W., Jr. *J. Phys. Chem.* **1990**, *94*, 8500.

(9) For example, *Catalytic Activation of Carbonic Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*; Aresta, M., Schloss, J. V., Eds.; Kluwer Academic Publishers: Boston, 1990.

(10) Fehsenfeld, F. C.; Fergusson, E. E. *J. Chem. Phys.* **1974**, *61*, 3181.

Table I.[a] Rate Constant for the Reaction of $O^-(H_2O)_n$ with CO_2 at $T = 300$ K

n	this work	reported[10]	theory[18]
0	*b*	*c*	11.6
1	8.5	8.2	9.1
2	7.8	7.9	8.2
3	6.9		7.7

[a] Units 10^{-10} cm^{-3}/s. [b] $k(3) = 1.7 \times 10^{-28}$ cm^6/s. [c] $k(3) = 1.5 \times 10^{-28}$ cm^6/s.

mined the reaction of $O_2^-(H_2O)_n$ with n extended up to 4. Hierl et al.[12] studied the energy dependence of the cross sections for the reactions of $OH^-(H_2O)_{n=0-3}$. Additionally, Viggiano et al.[13] recently studied the temperature dependence of rate constants for the reaction of $O^-(H_2O)_{n=0-2}$. All these investigations deal with small hydrated clusters, which essentially display reactions expected for gas-phase species. For example, in ref 12, it was found that CO_2 replaces water molecules in the hydrated clusters $OH^-(H_2O)_{n=1-2}$ to form $HCO_3^-(H_2O)_m$ with a rate constant near the gas-phase collisional limit. Interestingly, when $n = 3$, the measured rate constant was reported to be significantly lower than the calculated value (the reason was not discussed in the paper). Obviously, in order to observe the effects of solvation that might eventually lead to an understanding of the condensed phase, studies of large clusters are needed.

In this paper, we report the cluster size dependence of rate constants and reaction mechanisms for the reaction of CO_2 with large hydrated anion clusters $X^-(H_2O)_{n=1-59}$, X = OH, O, O_2, and O_3. The effect of temperature on the rate constants for small clusters was also studied, and the results are reported herein. The possible applications of the present experimental results to an understanding of the enzymatic hydrolysis dynamics of CO_2 is also discussed.

Experimental Section

The experiment was performed on a fast-flow apparatus affixed with a high-pressure ion source and operated at both room and low temperatures. The instrumentation and experimental procedures have been described in detail in earlier publications.[14-17] Briefly, $OH^-(H_2O)_n$ and $O^-(H_2O)_n$ anion clusters are formed in the ion source by the discharge ionization of a water/helium mixture. Adding a small amount of O_2 into the source greatly enhances the intensity of $O_2^-(H_2O)_n$ and $O_3^-(H_2O)_n$ clusters. Thereafter, the clusters are carried by He from the ion source into the flow tube where they react with CO_2 that is diluted in He, and added into the flow tube through heatable reactant gas inlet.[14] The typical He flow rate is about 8000 standard cm^3/min, and the pressures in the ion source and the flow reactor are about 20 and 0.3 Torr, respectively. Most of the gas in the flow tube is pumped away by a roots pump; a small portion is sampled into the detection chamber where the reaction is quenched due to the large mean free path at the pressure existing there ($p < 1 \times 10^{-5}$ Torr), and the reaction products and unreacted parent ions are analyzed and monitored by using a quadrupole mass spectrometer and counted by an electron multiplier. The slope of a plot of the logarithm of the parent ion intensity versus the neutral reactant concentration yields the reaction rate constant, while mass scanning gives the reaction product distribution. The experimental conditions for a quantitative rate constant measurement, e.g., uniform temperature distribution along the flow tube, limiting the amount of water concentration in the flow tube and controlling the heating of the reactant gas inlet, have been discussed in ref 14. CO_2 is obtained from MG Industry Co., and used without further purification.

Table II.[a] Rate Constant for the Reaction of $OH^-(H_2O)_n$ with CO_2 at $T = 300$ K

n	this work	reported[10]	theory[18]
0	*b*	*c*	11.4
1	8.3		9.0
2	7.9	6	8.1
3	7.0	6	7.7
4		6	7.4

[a] Units 10^{-10} cm^3/s. [b] $k(3) = 2.7 \times 10^{-28}$ cm^6/s. [c] $k(3) = 2.5 \times 10^{-28}$ cm^6/s.

Table III.[a] Rate Constant for the Reaction of $O_2^-(H_2O)_n$ with CO_2 at $T = 300$ K

n	this work	reported[11]	theory[18]
0		*b*	9.4
1	5.9	>5.2 ($T = 295$)	8.4
2	0.9	0.7 ($T = 292$)	7.8
3		$<1 \times 10^{-2}$ ($T = 187-213$ K)	7.5
4		$<1 \times 10^{-2}$ ($T = 187-213$ K)	7.3

[a] Units 10^{-10} cm^3/s. [b] Values of $k(3) = 4.7 \times 10^{-28}$ and 1.5×10^{-28} cm^6/s are reported by Fehsenfeld and Ferguson,[10] and by Melton,[6] respectively.

Table IV.[a] Rate Constants for the Reactions of $O_3^-(H_2O)_n$ with CO_2 at $T = 300$ K

n	this work	reported[10]	theory[18]
0	6.9	5.5	8.4
1	4.6	3.5	7.9
2		<1.0	7.5

[a] Units 10^{-10} cm^3/s.

Results

(1) Rate Constant Measurement. The rate constants were measured at three different temperatures. At room temperature, only small clusters $OH^-(H_2O)_{n=0-3}$, $O^-(H_2O)_{n=0-3}$, $O_2^-(H_2O)_{n=0-2}$, and $O_3^-(H_2O)_{n=0-1}$ are produced, and hence these are the only ones that could be studied at this temperature. The measured rate constants are summarized in Tables I–IV. The unsolvated ions OH^- and O^- only very slowly react with CO_2, and the rate constants show a linear dependence on flow tube pressure. The third-order rate constants are 2.7×10^{-28} and 1.8×10^{-28} cm^6/s, respectively, which agree very well with the values reported by Fehsenfeld and Ferguson.[10] Reaction of bare ion O_2^- with CO_2 is also very slow. But, the rate constant is very difficult to obtain accurately due to large curvature in the rate plot, which might be caused by the interference of reactions of other cluster ions coexisting in the flow tube.[10] Since the rate constant of this reaction has been measured before,[6,10] and the focus of our attention was on studies of large clusters, no further effort was given to this reaction, which probably can be more appropriately determined by using the selected ion flow tube (SIFT) technique.[17] Our findings show that O_3^- reacts with CO_2 at near the collision limit as listed in Table IV; the reaction mechanism is discussed later in the text.

For the solvated cluster ions, as presented in Tables I–IV, the rate constants are very close to the Langevin collision limit.[18] The measured rate constants have a negative dependence on the square root of the reduced mass of the collision complex as predicted by theory. The agreement between our experimental results and previously reported values are very good, as is the agreement with Langevin calculations. In the case of small cluster ions, the solvation effect of water molecules on the reactivity of O_2^- and O_3^- ions is much larger than that of O^- and OH^-; i.e., the measured rate constants drop much faster than the theoretical prediction as the cluster size increases. This phenomenon can be understood in terms of the thermochemistry of the reactions as discussed later in the text.

Since CO_2 has no permanent dipole moment, on the basis of Langevin theory, those reactions that proceed at near the gas-phase

---

(11) Fahey, D. W.; Bohringer, H.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1982**, *76*, 1799.

(12) Hierl, P. M.; Paulson, J. F. *J. Chem. Phys.* **1984**, *80*, 4890.

(13) Viggiano, A. A.; Morris, R. A.; Deakyne, C. A.; Dale, F.; Paulson, J. F. *J. Phys. Chem.* **1990**, *94*, 8193.

(14) Yang, X.; Zhang, X.; Castleman, A. W., Jr. Kinetics and Mechanism Studies of Large Protonated Water Clusters, $H^+(H_2O)_{n=1-60}$, at Thermal Energy. *Int. J. Mass Spectrom. Ion Processes*, in press.

(15) Yang, X.; Castleman, A. W., Jr. Temperature and Cluster Size Dependence Studies of Reactions of Protonated Water Clusters with Acetonitrile. *J. Chem. Phys.* **1991**, *95*, 130.

(16) Yang, X.; Castleman, A. W., Jr. *J. Phys. Phys.* **1990**, *93*, 2405.

(17) Passarella, R.; Yang, X.; Castleman, A. W., Jr. *Int. J. Mass Spectrom. Ion Processes* **1990**, *97*, 125.

(18) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

Table V.[a] Rate Constants for the Reactions of CO_2 at $T = 200$ K

	ion			
n	$OH^-(H_2O)_n$	$O^-(H_2O)_n$	$O_2^-(H_2O)_n$	$O_3^-(H_2O)_n$
0	*b* (11.4)[d]	*b* (11.6)	*b* (9.4)	6.8 (8.4)
1	8.3 (9.0)	8.6 (9.1)	5.2 (8.4)	5.8 (7.9)
2	7.8 (8.1)	8.4 (8.2)	0.8 (7.8)	*c* (7.5)
3	6.2 (7.7)	7.3 (7.7)	*c* (7.5)	*c* (7.3)
4	4.7 (7.4)	5.6 (7.4)	*c* (7.3)	*c* (7.1)

[a] Units for all the rate constants are 10^{-10} cm/s. [b] Temperature dependence for these association reactions has been reported. [c] $k < 1 \times 10^{-12}$ cm³/s at a flow tube pressure of about 0.3 Torr. [d] Numbers in parenthesis are calculated values.

Table VI.[a] Rate Constants for the Reactions of CO_2 at $T = 130$ K

	ion			
n	$OH^-(H_2O)_n$	$O^-(H_2O)_n$	$O_2^-(H_2O)_n$	$O_3^-(H_2O)_n$
0	*b*	*b*	*b*	8.0
1	8.7	8.9	6.6	7.0
2	8.4	8.5	1.0	*c*
3	7.5	7.9	*c*	*c*
4	6.1	6.7	*c*	*c*
5	4.5	4.8	*c*	*c*
6	4.3	3.8	*c*	*c*
7	2.8	3.2	*c*	*c*
8	2.2	2.6	*c*	*c*
9	2.0	1.8	*c*	*c*
10	1.8	1.5		*c*
11	0.80	1.2		*c*
12	0.72	0.93		*c*
13	0.52	0.42		*c*
14	0.19	0.42		*c*
15	0.16	0.27		

[a] Units for all the reactions are 10^{-10} cm/s. [b] Temperature dependence for these association reactions has been reported. [c] $k < 1 \times 10^{-12}$ cm³/s at a flow tube pressure of about 0.3 Torr.

collision limits should not display any temperature dependence.[18] The experimental findings are in accordance with the theoretical predictions. As listed in Table V, at a temperature of about 200 K, the measured rate constants are very close to the values measured at room temperature. The difference between experimentally measured rate constants and the theoretical calculation gets larger as cluster size increases; the reason is discussed later in the text. See Tables I–IV.

Large cluster anions do not appear until the temperature is decreased below about 140 K. Table VI summarizes all the rate constants for the clusters with *n* up to 15 measured at $T = 130$ K. Again, for small cluster sizes, temperature has little effect on the rate constants. However, cluster size does have a strong effect on the rate constants; in the case of the $OH^-(H_2O)_n$ and $O^-(H_2O)_n$ clusters, the rate constants decrease with increasing cluster size much faster than the theoretically predicted collision rates; see Figure 1. For clusters larger than $n = 15$, the reactions become too slow to measure accurately, which can be seen clearly in Figure 3 where the intensity of large parent $OH^-(H_2O)_n$ clusters is observed to remain essentially unchanged as CO_2 is added into the flow reactor. At low temperatures, $O_2^-(H_2O)_{n=1-2}$ and $O_3^-(H_2O)_{n=0-1}$ react with CO_2 with rate constants very similar to those measured at room temperature. For the larger clusters $O_2^-(H_2O)_{n>2}$ and $O_3^-(H_2O)_{n>1}$, the rate constants are too small to be measured accurately, and only an upper limit is given in Table VI.

(2) Reaction Mechanisms. For small clusters at room temperature, the reaction mechanisms have been well established.[10-13] It has been found that OH^-, O^-, and O_2^- react with CO_2 via an association mechanism:

$$OH^- + CO_2 + He \rightarrow HCO_3^- + He \tag{1}$$

$$O^- + CO_2 + He \rightarrow CO_3^- + He \tag{2}$$

$$O_2^- + CO_2 + He \rightarrow CO_4^- + He \tag{3}$$

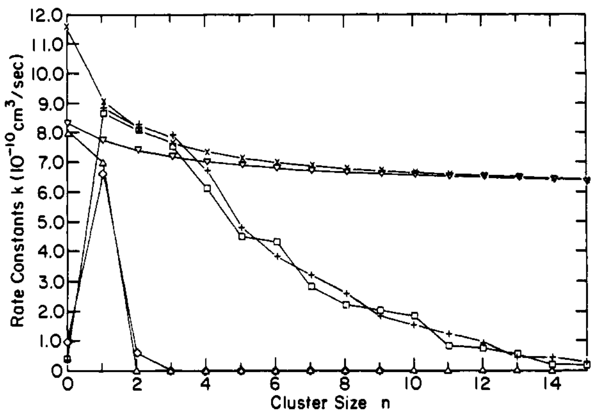

Figure 1. Cluster size dependence of the rate constants for the reactions of CO_2 with the large hydrated anions at $T = 130$ K. Experimental values: □ for $OH^-(H_2O)_n$, + for $O^-(H_2O)_n$, ◇ for $O_2^-(H_2O)_n$, and △ for $O_3^-(H_2O)_n$. Theoretical values: x for $O^-(H_2O)_n$ and ▽ for $O_3^-(H_2O)$; calculated values of $OH^-(H_2O)_n$ and $O_2^-(H_2O)_n$ are between the two lines.

where He acts as the third-body for the stabilization of the collision complexes in these reactions. Since these reactions are much slower than those of the hydrated ions at room temperature, the intensity of the bare ions remains almost unchanged in the product distribution; see Figure 2.

The hydrated anion clusters can, on the other hand, react with CO_2 by a ligand substitution mechanism, e.g.

$$OH^-(H_2O)_n + CO_2 \rightarrow HCO_3^-(H_2O)_{n-1} + H_2O \tag{4}$$

Since the bonding of CO_2 with OH^- and O^- is very strong (the reaction enthalpies are −88 and −50 kcal/mol, respectively,[19] the release of the excess energy during reaction can "boil" more than one water molecule from the reaction products.[12] Instead of proceeding as in reaction 4, the following reaction mechanisms are more likely for the reaction of hydrated OH^- and O^- clusters:

$$OH^-(H_2O)_n + CO_2 \rightarrow HCO_3^-(H_2O)_m + (n - m)H_2O \tag{5}$$

$$O^-(H_2O)_n + CO_2 \rightarrow CO_3^-(H_2O)_m + (n - m)H_2O \tag{6}$$

As seen in Figure 2, evidence for the proposed mechanism comes from observations that the major reaction products are HCO_3^- and CO_3^- at room temperature, and in the case of the larger clusters studied at low temperature, the product species are solvated by only a few water molecules; see Figure 3.

The reaction mechanism for $O_3^-(H_2O)_n$ is somewhat different from reactions 5 and 6. It was found[10] that it is the O_2 molecule, instead of water, which is replaced by CO_2:[10]

$$O_3^-(H_2O)_n + CO_2 \rightarrow CO_3^-(H_2O)_m + O_2 + (n - m)H_2O \tag{7}$$

This mechanism is supported by the present experiments which show that no reaction products of the form of $CO_3^-(H_2O)_nO_2$ occur in the products; see Figure 2.

Discussion

(1) Solvation Effect. Hydration has a pronounced effect on the reaction thermodynamics of $O_2^-(H_2O)_n$ and $O_3^-(H_2O)_n$. Indeed, the clustering of only one or two water molecules makes the reaction endothermic for $O_2^-(H_2O)_n$ and $O_3^-(H_2O)_n$ as shown in Table VII.

However, for $OH^-(H_2O)_n$ and $O^-(H_2O)_n$, due to the formation of very stable products, namely, $HCO_3^-(H_2O)_m$ and $CO_3^-(H_2O)_m$, the reaction enthalpy is still very exothermic even when three water ligands are replaced by one CO_2 molecule. In fact, the enthalpy change approaches nearly a constant value as cluster size increases. Values are listed in Table VIII for the reaction of CO_2 with $OH^-(H_2O)_n$. There is a paucity of thermodynamic data in the

---

(19) Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

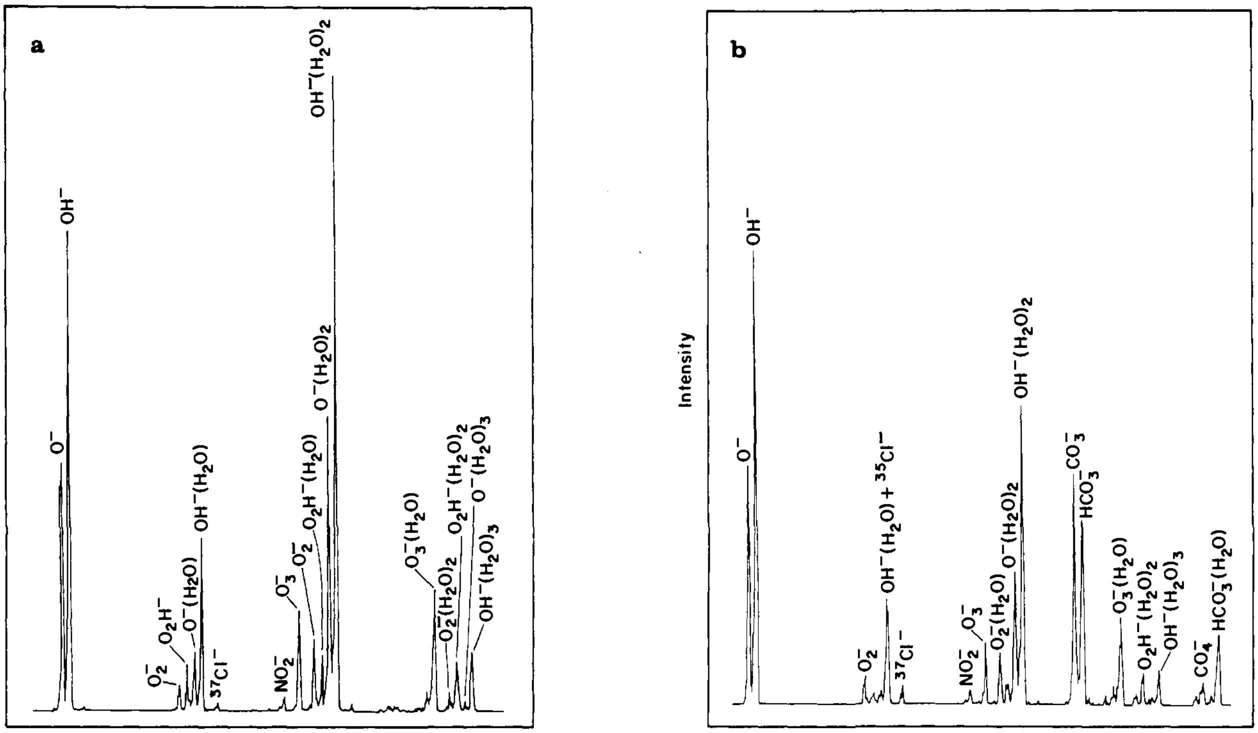

Figure 2. Mass spectra for the (a) parent cluster ion and (b) products of the reactions of hydrated anion clusters with CO_2 at room temperature.

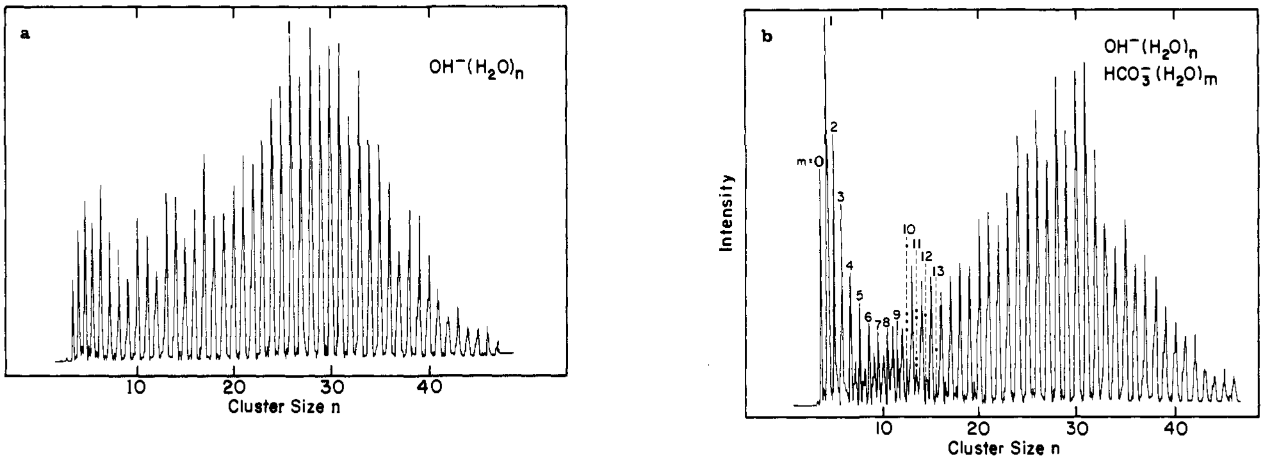

Figure 3. Mass spectra for the (a) parent cluster ions and (b) products of the reactions of large hydrated anion clusters $OH^-(H_2O)_n$ with CO_2 at $T = 130$ K.

Table VII.[a] Enthalpy Changes $\Delta H°$[b] for the Reactions

$$O_2^-(H_2O)_n + CO_2 \rightarrow CO_4^-(H_2O)_{n-1} + H_2O$$

$$O_3^-(H_2O)_n + CO_2 \rightarrow CO_3^-(H_2O)_{n-1} + O_2 + H_2O$$

	n			
X	0	1	2	3
O_2	-18.4	0	2.6	7.4
O_3	>-20	*c*	*c*	*c*

[a] All the values in this table are cited or derived on the basis of ref 19 and references therein. [b] Units kilocalories per mole. [c] No data available in the literature.

literature for reactions of $O^-(H_2O)_n$ with CO_2. However, since the hydration bond energies are very similar for OH^- and O^- and for HCO_3^- and CO_3^-, similar thermodynamic behavior is expected for the reactions of $O^-(H_2O)_n$ and CO_2 and $OH^-(H_2O)_n$ with CO_2 as a function of cluster size. Thus, the explanation for the discrepancy between the experimentally measured rate constants and the theoretically predicted values, shown in Figure 1, have to be accounted for in terms of the reaction kinetics.

From the point of view of chemical kinetics, an association reaction at thermalized conditions can be described by a few elementary molecular processes via the following mechanism:

$$CO_2 + OH^-(H_2O)_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{OH^-(H_2O)_n(CO_2)\}^* \quad (8)$$

$$\{OH^-(H_2O)_n(CO_2)\}^* + He \xrightarrow{k_2} OH^-(H_2O)_n(CO_2) + He \quad (9)$$

$$\{OH^-(H_2O)_n(CO_2)\}^* \xrightarrow{k_r} HCO_3^-(H_2O)_m + (n-m)(H_2O) \quad (10)$$

By this mechanism, when CO_2 collides with $OH^-(H_2O)_n$ anions, the reaction intermediates $\{OH^-(H_2O)_n(CO_2)\}^*$ are formed at first. These reaction intermediate complexes can undergo three further reactions: unimolecular dissociation (k_{-1}) back to the original reactants, collisional stabilization (k_2) via a third-body, namely, He, and intermolecular reaction (k_r) to form stable products $HCO_3^-(H_2O)_m$ with the concomitant displacement or evaporative loss of water molecules.

By using a steady-state approximation on the concentration of $\{OH^-(H_2O)_nCO_2\}^*$, the experimentally measured rate constant,

Table VIII.[a] Enthalpy Changes ΔH°[b] for the Reaction

$$OH^-(H_2O)_n + CO_2 \rightarrow HCO_3^-(H_2O)_{n-m} + m(H_2O)$$

	m			
n	0	1	2	3
0	-88			
1	-82	-66		
2	-80	-65	-49	
3	-79	-65	-50	-34
4	-78	-64	-50	-35
5	-78	-63	-51	-36

[a] All the values in this table are cited or derived on the basis of ref 19 and references therein. [b] Units kilocalories per mole.

k_{exp}, can be related to the rate constants of the elementary steps by the following equation:

$$k_{exp} = k_1\{k_2[He] + k_r\}/\{k_{-1} + k_2[He] + k_r\} \quad (11)$$

Equation 11 can be simplified under the following four possible limiting situations: (i) $k_r \gg k_2[He]$ and k_{-1}; then

$$k_{exp} = k_1 \quad (12)$$

(ii) $k_2[He] \gg k_r$ and k_{-1}; then

$$k_{exp} = k_1 \quad (13)$$

(iii) $k_{-1} \gg k_r$ and $k_2[He]$, and $k_2[He] \gg k_r$; then

$$k_{exp} = k_1k_2[He]/k_{-1} \quad (14)$$

(iv) $k_{-1} \gg k_r$ and $k_2[He]$, and $k_r \gg k_2[He]$; then

$$k_{exp} = k_1k_r/k_{-1} \quad (15)$$

In the present experiments, no systematic pressure dependence on k_{exp} was found in the pressure range of about 0.3–0.6 Torr, which eliminates the possibility of case iii. Since CO_2 has no permanent dipole moment, the bonding between CO_2 and the anion clusters is expected to be weak and hence case ii is not likely. This is further supported by the experimental observation that the products $HCO_3^-(H_2O)_m$ have far fewer water ligands than the parent $OH^-(H_2O)_n$. In other words, if the association channel were important, the product distribution should be similar to that of the parent ions. Thus, only two possibilities are left, namely, cases i and iv. Interestingly, this prediction matches very well with the present experimental observations because, as seen in Figure 1, at small cluster size ($n \leq 3$), k_{exp} is very close to k_1. This should be expected since the reaction is a ligand-switching ion-molecule reaction that usually has no reaction barrier; thus, case i dominates the reaction mechanism for smaller anion clusters. Referring again to Figure 1, as cluster size increases, k_{exp} decreases much faster than k_1. Under this condition, case iv is expected to be of increasing importance since, as the number of water ligands increases, the bonding between (as an association complex) CO_2 and the anionic cluster gets weaker, which could lead to an increase of k_{-1} even though the number of oscillators is increasing. It is likely that, as the number of water ligands around OH^- increases, similar to that in aqueous solutions, a reactive encounter between CO_2 and OH^- gets more difficult within the reaction intermediate $\{OH^-(H_2O)_n(CO_2)\}^*$ during the residence time in the flow reactor. Thus, under such conditions, k_{exp} should be expressed better by eq 15 than by 12. The rate constant k_{-1} may eventually reach a nearly constant value while k_r continues to diminish with an increasing degree of clustering.

Interestingly from eq 15, the ratio of k_{exp} and k_1 for large cluster sizes equals the ratio of k_r and k_{-1}:

$$k_{exp}/k_1 = k_r/k_{-1} \quad (16)$$

The present experiments are not designed for evaluating the absolute values of k_r and k_{-1}. However, if either one of the rate constants can be obtained experimentally or theoretically, e.g., RRKM calculation for k_{-1},[15] it is straightforward to get the order one by using eq 16.

(2) Enzymatic Hydrolysis Dynamics of CO_2. The present experiment results are of direct interest in further unraveling the details of the enzymatic hydrolysis dynamics of CO_2. In order to demonstrate how this can be accomplished, we begin with the simplest situation: solvation of CO_2 in water.

It is well-known that CO_2 reacts very slowly with pure water to form carbonic acid:

$$CO_2(aq) + H_2O(aq) \xrightarrow{k_{H_2O}} H_2CO_3(aq) \quad (17)$$

with a second-order rate constant, k_{H_2O}, of about 7×10^{-4} M^{-1} s^{-1},[20] or 1×10^{-24} cm^3 s^{-1}. The slow reaction may be partly due to the large reaction barrier, about 52 kcal/mol, for the reaction of CO_2 with H_2O.[21] H_2CO_3 can then readily disproportionate to give H^+ and HCO_3^-:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad (18)$$

with an equilibrium constant of 4.5×10^{-7} mol/L.[22]

In basic solutions, CO_2 can react directly with CO_2 to form HCO_3^-:

$$CO_2(aq) + OH^-(aq) \xrightarrow{k_{OH^-}} HCO_3^-(aq) \quad (19)$$

The second-order rate constant k_{OH^-} was measured to be 8.5×10^3 M^{-1} s^{-1},[23] about 7 orders of magnitude larger than k_{H_2O}, possibly due to the existence of only a low energy barrier to reaction.[24]

In most living systems, including both animals and plants, the hydrolysis of CO_2 and dehydration of HCO_3^- are apparently crucial in the respiration and acid–base balance processes. Since the environment of the biological systems is near neutral, a catalyst is required, and this is carried out efficiently by the enzyme carbonic anhydrase (CA). The rate constant for the enzymatic hydrolysis of CO_2 has been measured to be 7.5×10^7 M^{-1} s^{-1},[25] or 1.2×10^{-13} cm^3 s^{-1}, which is about 11 orders of magnitude larger than k_{H_2O}, and 4 orders of magnitude larger than k_{OH^-}. By contrast, the gas-phase collision limit for CO_2 with a large anion is about 10^{-10} cm^3 s^{-1}.

It has been found[26] that the key element of the catalytic effect of CA is due to a zinc ion that breaks a water molecule into H^+ and OH^-. The OH^- then reacts fast with CO_2 to form HCO_3^-. Now comes the following question: Why does the OH^- produced by CA react with CO_2 4 orders of magnitude faster than the OH^- in basic solution? In other words, how does the enzymatic catalysis take place?

By comparing the reactivity of CO_2 with H_2O and OH^- in the gas phase and in water with and without the carbonic enzyme, Jönsson et al. proposed[27] a reaction mechanism for the enzymatic catalysis by stating "*the enzyme would thus be an efficient catalyst if it could strip the OH^- of its solvation sphere and at the same time keep it stable relative to protonation*". Since this proposal is based on the results of considering the reactivity of anion OH^- in the gas phase compared to the solution phase, the information between the two phases is missing. In other words, there had been no direct evidence, showing how the transition takes place from the gas phase to the solution phase at different degrees of hydration of OH^-, to support the proposed mechanism.

In the present experiments, we started with OH^- ion. The experimental results show that bare OH^- reacts very slowly with CO_2 via an association mechanism to form HCO_3^-. However, when the OH^- is solvated by water ligands, the reaction mechanism changes to ligand switching. More interestingly, by varying the hydration with different water clusters, strong solvation effects

---

(20) Khalifah, R. G. *J. Biol. Chem.* **1971**, *246*, 2561.

(21) Jönsson, B.; Karlström, G.; Wennerström, H.; Roos, B. *Chem. Phys. Lett.* **1976**, *41*, 317.

(22) Bowers, V. E.; Bates, R. G. In *Handbook of Analytical Chemistry*; Meites, L., Ed.; McGraw-Hill Book Co.: New York, 1963.

(23) Martin, R. B. *J. Inorg. Nucl. Chem.* **1976**, *38*, 511.

(24) Pinsent, B. R. W.; Pearson, L.; Roughton, F. J. W. *Trans. Faraday Soc.* **1956**, *52*, 1512.

(25) Khalifah, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 1986.

(26) Woolley, P. *Nature* **1975**, *258*, 677.

(27) Jönsson, B.; Karlström, G.; Wennerström, H. *J. Am. Chem. Soc.* **1978**, *100*, 1658.

on the reactivity of OH^- due to the water ligands is observed as shown in Figure 1. Furthermore, by studying the reaction kinetics based on a Lindemann-type mechanism, we found that the solvation effect is caused by the increase of the unimolecular dissociation rate constant k_{-1} and by the decrease of the intermolecular conversion rate constant k_r as cluster size increases. Thus, from the present experiments, we obtain a similar conclusion as Jönsson et al. that since the reactivity of OH^- in the presence of CA is about 4 orders of magnitude higher than in basic aqueous solution without CA, and the higher degree of hydration causes more of a drop in the reactivity of the OH^- anion, *the enzymatic effect of CA is likely to be accomplished by decreasing the hydration of* OH^-. Hence, despite the rather different conditions, the present experiment provides some experimental support for the proposed mechanism, and offers an example of how cluster research can bridge the gap between the gas and condensed phases.

Conclusion

Studies of the reaction kinetics of large hydrated anion clusters $X^-(H_2O)_{n=1-59}$ with CO_2 in the gas phase at different temperatures and pressures reveal the following.

(1) The reactions of small hydrated anionic clusters $OH^-(H_2O)_n$ and $O^-(H_2O)_n$ with CO_2 show no large dependence on the flow tube pressure and temperature due to the nature of the ligand-switching reaction mechanism and the lack of a permanent dipole of carbon dioxide, which is similar to what has been reported in the literature. However, the present work demonstrates that the reaction rate constants drop very quickly as the cluster sizes increase, due mainly to the solvation effect caused by the weak bonding of CO_2 to the anion clusters.

(2) Hydration has a large effect on the reaction thermodynamics of O_2^- and O_3^-. Only one and two water ligands make the reactions endothermic even at low temperatures.

The results yield experimental evidence in support of the mechanism which has been proposed to account for the enzymatic hydrolysis of CO_2, one that is believed to be catalyzed by carbonic anhydrase. The hydrolysis of CO_2 in many biological systems may occur by the creation of a hydrophobic environment so that the hydration of the OH^- ion is greatly reduced, which enhances the interaction between CO_2 and the anion, and increases the intermolecular conversion rate constant for the formation of $HCO_3^-(H_2O)_m$.

It is well established that CO_2 plays an important role in many atmospheric and environmental processes both physically, e.g., the green house effect, and chemically like in the negative ion chemistry of the stratosphere.[3] Since more hydration occurs in lower parts of the atmosphere, the reactivity of large hydrated clusters, charged or neutral, is of interest in understanding the chemistry of CO_2 in the atmosphere. In another paper,[28] the chemistry between large hydrated clusters and CO_2 with regard to the atmospheric and environmental applications will be discussed.

Acknowledgment. The financial support of the National Science Foundation, Grant No. ATM-90-15855, is gratefully acknowledged.

---

[28] Yang, X.; Castleman, A. W., Jr. To be published.

Isotopomer Distributions of Neutral Products from a Doubly Labeled Cation in the Gas Phase. Interconversion of 1-Fluoro-1-propyl Cation and 1-Fluoroisopropyl Cation on the $C_3H_6F^+$ Potential Energy Surface

Thomas A. Shaler and Thomas Hellman Morton*

Contribution from the Department of Chemistry, University of California,
Riverside, California 92521-0403. *Received July 30, 1990.*
Revised Manuscript Received March 28, 1991

Abstract: The title cations $CH_3CH_2CHF^+$ (**3**) and $CH_3CHCH_2F^+$ (**4**) are formed as transient intermediates in the gas phase. These are labile on the millisecond timescale as free ions but can be intercepted in ion–neutral complexes. When **3** is generated as a free cation by reaction of CF_3^+ with propionaldehyde, it rearranges to $(CH_3)_2CF^+$ (**1**), as shown by recovery of 2-fluoropropene as a neutral product from its deprotonation in an EBFlow experiment. The same neutral product is recovered when **1** is produced directly by reaction of acetone with CF_3^+ in the EBFlow. Neutral products indicative of **3** and **4** (allyl fluoride and 1-fluoropropene) are recovered when these cations are formed in $[R^+ PhO^\bullet]$ ion–neutral complexes by electron bombardment of CH_3CDFCH_2OPh (**6**). Analysis of the isotopic distribution in the recovered neutrals from EBFlow radiolysis of $CH_3CDF^*CH_2OPh$ (where the asterisked carbon is ^{13}C-labeled) allows an assessment of the primary rearrangement pathways. The distribution of label is assayed by using ^{19}F NMR. Rearrangement of the R^+ moiety to form deuterated **1** occurs in about half of the complexes formed. In the remainder, methyl transfer (to form deuterated **3**) is 2–3 times faster than fluoride transfer (to form deuterated **4**). Scrambling of deuterium in the neutral products provides evidence that **3** and **4** interconvert within the ion–neutral complexes.

Double isotopic labeling, using ^2H and ^{13}C specifically incorporated into a single molecule, has been employed for at least two decades as a mass spectrometric tool to investigate rearrangments of gaseous cations.[1] In addition to being heavier than the more common isotopes, both nuclei have nonzero spin. It is therefore conceivable to use magnetic resonance to probe the positions of labeled atoms in the reaction products in situations where mass spectrometry is unable to distinguish alternative pathways. Such an experiment can yield a wealth of information, provided that it is possible to resolve positional isomers in a product mixture.

We have reduced this idea to practice. This paper reports the use of the electron bombardment flow (EBFlow) technique[2] to

---

[1] Perry, W. O.; Beynon, J. H.; Baitinger, W. E.; Amy, J. W.; Caprioli, R. M.; Renaud, R. N.; Leitch, L. C.; Meyerson, S. *J. Am. Chem. Soc.* **1970**, *92*, 7236–7238.

[2] Morton, T. H. In *Techniques for the Study of Ion-Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; *Techniques of Chemistry XX*; Wiley-Interscience: New York, 1988; pp 119–164.

0002-7863/91/1513-6771$02.50/0