Yield determination of OH ($v=0,1$) radicals produced by the electron-ion recombination of protonated molecules

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A flowing afterglow apparatus in conjunction with laser induced fluorescence (LIF) diagnostics has been used to determine the yields of OH($X^2\Pi$, $v=0,1$) produced by the dissociative recombination (DR) of HCO_2^+, HN_2O^+, HCO^+ ions with electrons at 300 K. The yield for $v=0$ radicals was determined relative to the known OH yield from the recombination of H_3O^+ ions while the production of vibrationally excited OH in $v=1$ was obtained relative to that in $v=0$ by comparing LIF spectra. © *1997 American Institute of Physics.* [S0021-9606(97)04231-1]

I. INTRODUCTION

When Adams *et al.*[1] and Herd *et al.*[2] made the first measurements of OH yields from the recombination of protonated molecules such as H_3O^+, HN_2O^+, and HCO_2^+, they found a considerable amount of vibrational excitation in the OH product. In the preceding paper, we presented our flowing afterglow measurements of OH($X^2\Pi$, $v=0,1$) yields from the recombination of H_3O^+ ions[3] and the results confirmed Herd *et al.*'s work. However, when we extended these studies to HN_2O^+ and HCO_2^+ ions we found significantly lower yields of vibrationally excited OH. The results given here are based on a more thorough analysis of the kinetics of the recombining plasma and should be more reliable.

The energetically allowed channels[4] for recombination of HN_2O^+ and HCO_2^+ ions are:

$$HN_2O^+ + e \rightarrow \mathbf{OH} + N_2 + 10.42\ \text{eV} \quad (1a)$$

$$\rightarrow \mathbf{OH} + N + N + 0.66\ \text{eV} \quad (1b)$$

$$\rightarrow O + H + N_2 + 6.03\ \text{eV} \quad (1c)$$

$$\rightarrow NO + NH + 6.04\ \text{eV} \quad (1d)$$

$$\rightarrow NO + N + H + 2.77\ \text{eV} \quad (1e)$$

$$\rightarrow N_2O + H + 7.7\ \text{eV} \quad (1f)$$

and

$$HCO_2^+ + e \rightarrow \mathbf{OH} + CO + 6.86\ \text{eV} \quad (2a)$$

$$\rightarrow CO_2 + H + 7.92\ \text{eV} \quad (2b)$$

$$\rightarrow O + H + CO + 2.47\ \text{eV} \quad (2c)$$

$$\rightarrow O_2 + CH - 0.044\ \text{eV} \quad (2d)$$

with channel (2d) being slightly endothermic. For HCO^+ ions there are only two accessible channels:[4]

$$HCO^+ + e \rightarrow \mathbf{OH} + C + 0.75\ \text{eV} \quad (3a)$$

$$\rightarrow CO + H + 7.45\ \text{eV}. \quad (3b)$$

It must be noted here that in the most stable forms of these ions, the H atom is bonded to an oxygen atom in HN_2O^+ and HCO_2^+ but to C in HCO^+. There are no theoretical predictions for the products of HN_2O^+ and HCO_2^+ recombination although following Bates'[5] suggestion one could argue that channels (1f) and (2b) should be favored, while for HCO^+ ions extensive *ab initio* calculations of Kraemer and Hazi[6] suggest that H + CO should be the dominant channel.

II. EXPERIMENT

The flowing afterglow apparatus and associated methods were essentially identical to those described in the preceding article.[3] Typically, a large amount of H_2 ($\sim 10^{14}$ cm^{-3}) was used to convert the primary Ar^+ ions to H_3^+, and reagent gases CO_2, N_2O, CO and H_2O at concentrations of 1 to 10×10^{12} cm^{-3} were added to form the desired protonated species by proton transfer from H_3^+.

In addition to OH in the electronic ground state, excited OH($A^2\Sigma^+$) can also be produced by the recombination reactions (1a) and (2a). For instance, OH(A→X) emissions were observed in recombining HN_2O^+ and HCO_2^+ plasmas[7] and produced a constant background signal that had to be subtracted from the LIF measurements. With the exception of this higher emission background, the LIF observations of the OH products were very similar to those made in the case of H_3O^+.

Since we had previously determined the yield of OH ($v=0$) from the recombination of H_3O^+ ions (0.48 ± 0.07), this reaction was used as a reference source for OH($v=0$). The procedure was to first record the LIF signal arising from the ion under study, then to switch the reagent to H_2O and to record the LIF signal due to H_3O^+ recombination under otherwise unchanged conditions. The mass spectrometer was used to verify that no traces of the previously used reagent were left.

The numerical model[3] used to analyze the data differed only in the choice of input parameters from that described previously: these include ion-molecule reaction rate coefficients and diffusion coefficients. In the course of this work,

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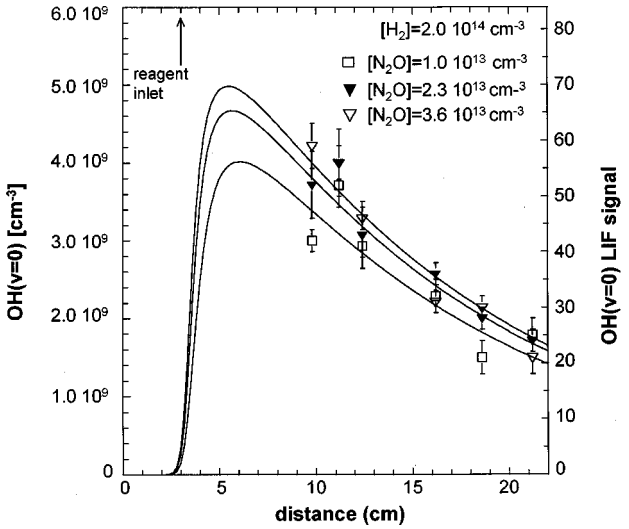

FIG. 1. OH($v=0$) LIF data (fluorescence photon counts per 100 laser shots) obtained for N_2O/H_2 reagent gases. The solid lines are model generated OH distributions (using a yield of 0.18 for the OH($v=0$) production from the recombination of HN_2O^+ ions) and the three data sets have been normalized to the model predictions by a common factor.

we remeasured the total recombination coefficients[8] for HCO_2^+, HCO^+ and HN_2O^+ ions. The measured values (4.6×10^{-7}, 1.9×10^{-7} and 4.5×10^{-7} cm^3 s^{-1}, respectively) agree rather well with earlier work and have been published elsewhere.[8]

III. RESULTS

As discussed earlier, the OH($X^2\Pi$, $v=0 \rightarrow A^2\Sigma^+$, $v=0$) LIF signal was recorded for different reagent gas concentrations for both the reference H_3O^+ and for the ion species under study. Typical data sets for HCO_2^+ and HN_2O^+ ions are shown in Figs. 1 and 2, together with fits using the

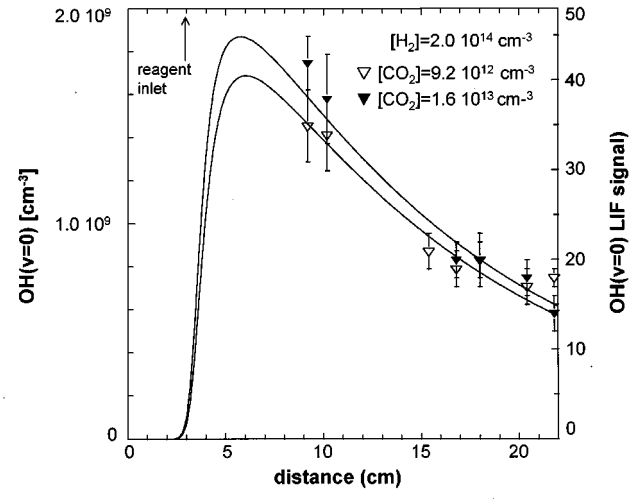

FIG. 2. OH(v=0) LIF data (fluorescence photon counts per 100 laser shots) obtained for CO_2/H_2 reagent gases. The solid lines are model generated OH distributions (using a yield of 0.08 for the OH($v=0$) production from the recombination of HCO_2^+ ions) and the two data sets have been normalized to the model predictions by a common factor.

TABLE I. Comparison between the OH yields obtained in this work and those of Herd *et al.* (HN_2O^+ and HCO^+ ions) and Adams *et al.* (HCO_2^+ ions).

ion	$f_{OH(v=0)}$		$f_{OH(v=1)}$	
	This work	Herd *et al.* Adams *et al.*	This work	Herd *et al.*[a] Adams *et al.*[a]
HN_2O^+	0.18±0.03	0.14±0.02	0.05±0.01	0.17±0.03
HCO_2^+	0.09±0.02	0.17±0.03	0.03±0.01	0.17±0.03
HCO^+	<0.02	-	-	-

[a]The results of Herd *et al.* and Adams *et al.* refer to $f_{OH(v>0)}$.

numerical model. In the data analysis the previously derived H_3O^+ yield of 0.48±0.07 was used and the yield of OH from the recombination of the target ion (HCO_2^+, HCO^+ or HN_2O^+) was varied until a best fit to experimental observations was achieved. The quoted uncertainties are standard deviations from the mean value. The yields listed in Table I are based on three different data sets of about 40 points each for HCO_2^+ and HN_2O^+ ions. For HCO^+ ions only one experiment was carried out in which only a minute amount of OH($v=0$) was observed (about 2 counts per 50 laser shots above background).

The yield of OH($v=1$) was determined relative to that of the vibrationally relaxed OH by comparing OH LIF spectra recorded for the same lines of the (0,0) and (1,1) bands for the OH($X^2\Pi\rightarrow A^2\Sigma^+$) transition. The spectral features were identical to those obtained from H_3O^+ recombination, but the (1,1) bands from HCO_2^+ and HN_2O^+ recombination were much weaker under all conditions. The yields of OH, $v=1$ (average of four experiments for each ion) are included in Table I. The uncertainties include the propagated errors from all numbers involved in the calculations.

IV. DISCUSSION

Our experimental technique was tested previously by determining the OH($v=0,1$) yield from the recombination of H_3O^+ ions. In that case, our results confirmed those obtained by Herd *et al.*[2] and Adams *et al.*,[1] an indication that both methods of obtaining and analyzing the data are valid. Using the same technique we derived yields for OH($v=0,1$) produced by the recombination of HCO_2^+, HCO^+ and HN_2O^+ ions. As can be seen in Table I there is good agreement only between the OH($v=0$) yields from HN_2O^+ but our OH ($v=0$) yield from HCO_2^+ is smaller by nearly a factor of 2 than the earlier result. Our measured OH($v=1$) yields are far smaller (by factors of 3–5) than the earlier data for OH ($v\geqslant1$). This might simply indicate that the earlier OH($v\geqslant1$) yields include a large contribution from $v\geqslant2$ but we do not believe that this interpretation is valid. Rather, we suggest that the methods used by Herd *et al.*[2] and by Adams *et al.*[1] may have been subject to some complications. Those authors made use of the known property of OH($v>0$) to vibrationally relax in collisions with NO. Thus, they added NO downstream of the main reagent inlet but upstream of the LIF port and observed an increase of the OH($v=0$) LIF signal which was attributed to the quenching of OH($v\geqslant1$) to

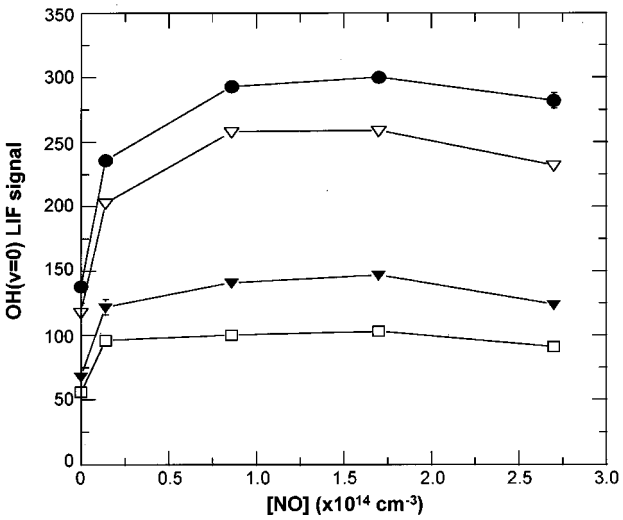

FIG. 3. Variation of the OH($v=0$) LIF signal (fluorescence photon counts per 100 laser shots) with the NO concentration added in the afterglow for HN_2O^+ ions. The four data sets refer to observations at different distances from the reagent inlet (filled circles: 5 cm, open triangles: 7 cm, filled triangles: 12 cm, open squares:15 cm).

the ground state. A comparison of the LIF signals with and without NO addition provided the yield for OH($v \geqslant 1$). They assumed that the NO addition led only to the quenching of the vibrationally excited OH without changing the ion chemistry of the system in any way.

To clarify the situation, we repeated their experimental procedure of adding NO for the derivation of the OH($v>0$) yields and to our surprise we observed a large increase in the OH($v=0$) LIF signal for both HN_2O^+ and HCO_2^+ ions (see Figs. 3 and 4) which would result in a yield of

$$f = 0.22 \pm 0.04$$

and

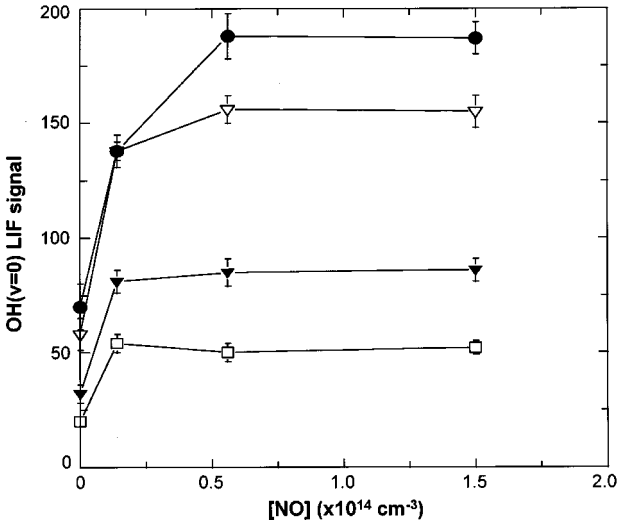

FIG. 4. Variation of the OH($v=0$) LIF signal (fluorescence photon counts per 100 laser shots) with the NO concentration added in the afterglow for HCO_2^+ ions. (filled circles: 5 cm, open triangles: 7 cm, filled triangles: 12 cm, open squares: 15 cm).

$$f = 0.18 \pm 0.02$$

for OH($v>0$) produced from the recombination of HN_2O^+ and HCO_2^+ ions respectively. However, the mass spectrometer indicated in both cases that addition of NO converted the terminal ion (either HN_2O^+ or HCO_2^+) into NO^+ ions. This suggested that the method of deducing OH($v>0$) concentrations by adding NO may have an undesired side-effect. In the studies of HN_2O^+ ions (i.e. $[NNOH]^+$) the data indicated that the reaction[4]

$$HN_2O^+ + NO \rightarrow NO^+ + \mathbf{OH} + N_2 + 1.15 \text{ eV} \quad (4)$$

occurs and leads to production of NO^+ and OH. It is possible that this reaction followed by vibrational relaxation accounts for most of the observed increase in OH($v=0$) rather than solely the quenching of OH($v>0$).

For HCO_2^+ ions the corresponding reaction[4]

$$HCO_2^+ + NO \rightarrow NO^+ + OH + CO - 2.40 \text{ eV} \quad (5)$$

is strongly endothermic but a two-step process consisting of the slightly endothermic reaction

$$HCO_2^+ + NO \rightarrow HNO^+ + CO_2 - (0.065 \pm 0.02) \text{ eV} \quad \text{(Ref. 9)} \quad (6)$$

followed by

$$HNO^+ + NO \rightarrow NO^+ + HNO + 0.94 \text{ eV} \quad (7)$$

can produce NO^+ ions. Further reaction of HNO with NO

$$HNO + NO \rightarrow \mathbf{OH} + N_2O + 0.71 \text{ eV} \quad (8)$$

probably produces the observed OH. The ion-molecule reactions involved in this scheme were studied in two separate experiments using the flow tube and a selected-ion drift tube. In the drift-tube experiment the intermediate HNO^+ product of reaction (6) was clearly observed. Rate coefficients for reactions (4) and (6) were measured in both the flowing afterglow and in the drift apparatus using well-established methods. Briefly, in the flowing afterglow the mass spectrometer was used to monitor the decay of the ion signal[10] (HN_2O^+ or HCO_2^+) as a function of the reagent gas (NO) concentration. In the drift tube experiment a known concentration of NO was added and the ion decay signal was recorded as a function of the residence time.[11] The agreement between the results obtained with the two methods was good and a rate coefficient of 6.0×10^{-11} cm^3/s was found for the reaction of HN_2O^+ ions with NO. For the reaction of HCO_2^+ ions with NO a rate coefficient of 2.0×10^{-11} cm^3/s was measured. The measured rate coefficients should be accurate to about 30%.

Another possible source for the excess OH observed by the addition of NO is provided by reactions (1d) and (2d). NH (Ref. 12) and CH (Ref. 13) are known to react with NO to produce OH

$$NH + NO \rightarrow \mathbf{OH} + N_2 + 4.38 \text{ eV} \quad \text{(yield 0.23)} \quad (9)$$

and

$$CH + NO \rightarrow \mathbf{OH} + CN + 2.23 \text{ eV}. \quad (10)$$

NH emissions have been observed in a HN_2O^+ afterglow by Foley *et al.*[7] but the small yield in reaction (9) makes it a minor contribution. We tried to detect the CH product of HCO_2^+ recombination using LIF but we could detect only traces of it. Thus, reaction (10) has no effect and channel (2d) can be disregarded. The structure of the HCO_2^+ ion is $[HOCO]^+$ which requires a major rearrangement of the atoms in the intermediate complex for the formation of CH.

We conclude that part of the OH ($v=0$) observed in the present experiment when NO was added resulted from the side-reactions described above. We, therefore, prefer our direct measurements of the OH($v=1$) yield. It is of interest to consider whether the earlier measurements of Adams *et al.* were affected in the same way. These authors were concerned about possible effects of NO addition on the ion chemistry and they tried to minimize these by adding the NO at a point where ''all of the recombination had occurred.'' Unfortunately, the distance between the CO_2 and the NO inlets was not stated[1] and cannot be ascertained;[14] thus it is not possible to estimate the importance of the residual ion-molecule reactions in that experiment.

Adams *et al.*[15] also used both LIF and VUV absorption to detect the H product from reaction (1) and they found an average yield of 0.84 ± 0.14 for the HN_2O^+ ions. Combining their H-atom yield and our OH yield of 0.23 ± 0.03 we conclude that channel (1d) (NH production) is a minor one.

For the HCO^+ both this and previous work[16] indicate a very small yield of OH, which agrees with the theoretical predictions of Kraemer and Hazi[6] who suggest that the recombination of this ion can only lead to the production of H + CO.

The state of internal excitation for the various ions is generally not clear. It is known that addition of a sufficient amount of the reagent gas results in the quenching of the internal excitation of the ions. Measurements of the recombination coefficients for different reagent concentrations did not result in more than 15% variation indicating that the ions are probably in their ground state.

V. CONCLUSIONS

The flowing afterglow technique combined with computer modeling has been used for the determination of absolute yields for the production of OH($v=0,1$) from the electron-ion dissociative recombination of HCO_2^+, HN_2O^+, and HCO^+ ions. The previously determined OH($v=0$) yield for the recombination of H_3O^+ ions has been used as reference. For OH($v=0$) the results are, in part, in good agreement with those obtained previously by Herd *et al.* and Adams *et al.*, but for OH($v=1$) our yields are much lower than theirs for OH ($v>0$). We suggest that the methods used by those authors for the determination of OH($v>0$) yields may include contributions from extraneous reactions that were not accounted for, but the situation is far from clear.

ACKNOWLEDGMENTS

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