absorption cross section for CIO is also critical for k_3 , but measurements of ClO kinetics in the present apparatus have been found repeatedly to be consistent with the concensus value for σ_{CIO} at the wavelength and spectral parameters used for monitoring ClO.

Discussion

The results obtained in this study provide evidence for the formation of ClO in the photolysis of Cl₂-ClONO₂ mixtures, and the kinetic behavior of ClO and NO3 is consistent with the occurrence of reactions 2 and 3 as postulated in our previous paper.⁷ The value of the overall rate coefficient for reaction 3 at 300 K, $k_{3a} + k_{3b} = 4.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ is in good agreement}$ with that reported previously by us, i.e., $(4.0 \pm 1.7) \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹ for 296 K, based on analysis of NO₃ kinetics only.

The results do not provide a definitive value for the branching ratio for the two exothermic channels 3a and 3b, but an upper limit value of $k_{3b}/k_{3a} < 0.4$ is indicated, i.e., $k_{3b} < 1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 300 K. No other measurements of these rate constants appear to have been reported. However the gas-phase reaction between OClO and NO2 has been studied¹¹ and a value for the temperature-dependent second-order rate constant reported: $k_{-3b} = 2.3 \times 10^{-14} \exp(-5388/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The final products of this reaction are $ClONO_2$ and N_2O_5 but it is probable that the reported Arrhenius expression relates to the reverse of reaction 3.¹¹ The most recent thermodynamic data for ClO, NO_2 , and OClO¹² and NO₃¹³ give $\Delta S_{3b}^{\circ} = 12.1 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_{3b}^{\circ} = -40.6 \text{ or } -48.8 \text{ kJ mol}^{-1}$, depending on whether the value of ΔH_{10}° (OClO) based on kinetic data¹⁷ or thermochemical measurement¹⁸ is used. The value of A_{3b} calculated from the relationship ln $A_{3b}/A_{-3b} = \Delta S_{3b}^{\circ}/R$ is 1.0×10^{-13} cm³ molecule⁻¹ s⁻¹ which, with

the above upper limit for k_{3b} at 300 K, gives $E_{3b} \ge 0$. This value is consistent with a value of $E_{3b} = 4.2 \text{ kJ mol}^{-1}$ indicated from the thermodynamic data using the higher value for $\Delta H_{\rm f}^{\circ}$ (OClO) together with kinetic data for the reverse reaction. The lower value of $\Delta H_{\rm f}^{\circ}$ (OClO) would give a negative value for $E_{\rm 3b}$ and require that reaction 3b was a major channel in the overall $ClO + NO_3$ reaction. On the whole, the weight of evidence suggests that reaction 3a is the major channel for the $ClO + NO_3$ reaction and that the small temperature dependence on the overall value of k_3 applies to this channel. A direct measurement of the OClO product from the reaction is clearly needed to establish the occurrence of reaction 3b.

The value obtained for k_2 is, within the experimental uncertainty, in agreement with our previously reported value of (7.6 \pm 1.1) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The observed lack of any temperature dependence over the rather limited temperature range is expected for a rapid atom-radical reaction of this type. One other measurement of k_2 using a similar technique to that employed by us has been reported,⁶ which is approximately a factor of 2 lower but with overlapping error limits: $k_2 = (2.7 \pm 1.0)$ \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. In view of the large uncertainty in k_2 from the present work (as discussed above) and in previous measurements, this rate constant cannot be considered well determined and further measurements are desirable.

Acknowledgment. This work was supported in part by the U.K. Department of Environment. We also thank Dr. G. S. Tyndall for helpful discussions.

Registry No. Cl₂, 7782-50-5; ClONO₂, 14545-72-3; N₂, 7727-37-9; Cl, 22537-15-1; NO₃, 12033-49-7; ClO, 14989-30-1.

Rate Constants for the Reaction $HO_2 + NO_2 + N_2 \rightarrow HO_2NO_2 + N_2$: The Temperature **Dependence of the Falloff Parameters**

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Rate constants for the title reaction were measured by flash photolysis ultraviolet absorption spectroscopy at N₂ pressures of 25, 50, and 100 Torr over the temperature range 228-358 K. The data were fit to an expression suitable for describing the pressure dependence of reactions in the falloff region with the temperature dependence of the falloff parameters given by $k_{0,N_2}(T) = k_{0,N_2}(300 \text{ K}) \{T/300\}^{-n}$ and $k_{\infty}(T) = k_{\infty}(300 \text{ K}) \{T/300\}^{-m}$. The inert gas pressures in this study were low enough to permit a precise determination of n (which describes the temperature dependence of the low-pressure, limiting third-order rate constant). The same rate constant data, however, were less sensitive to the determination of m (associated with the limiting high-presssure rate constant). For this reason, our final analysis utilizes a composite fit of our temperature dependent data along with similar data at 100 and 700 Torr of N₂ obtained by Sander and Peterson to yield $k_{0,N_2}(T) = 1.8 \times 10^{-31} \{T/300\}^{-(3.2\pm0.4)}$ cm⁶ molecule⁻² s⁻¹ and $k_{\infty}(T) = 4.7 \times 10^{-12} \{T/300\}^{-(1.4\pm1.0)}$ cm³ molecule⁻¹ s⁻¹.

Introduction

Formation of pernitric acid (HO_2NO_2) in the troposphere and stratosphere and its degradation via solar photolysis and chemical reaction play important roles in atmospheric chemistry.¹ Recognition of this importance has led to increased laboratory studies of the photochemistry and reaction dynamics of this species. In this regard, we recently reported² the results of a room temperature investigation of the pressure dependence of the rate constant for HO_2NO_2 formation (i.e., the gas-phase combination reaction between the hydroperoxy radical (HO₂) and nitrogen dioxide (NO_2) , reaction 1). The rate constant data (obtained at pressures

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M \quad (M = N_2, O_2)$$
 (1)

between 25 and 600 Torr) were parameterized according to the recommendations of Troe³ for reactions whose pressure-dependent kinetics are in the falloff region. These results have resolved some minor disparities among the existing literature reports^{4,5} and supported ref 5 as the primary experimental data base upon which recommendations have been made for use in atmospheric mod-

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eling.⁶ However, data on the temperature dependence of reaction 1 as a function of pressure are quite limited (the only measurements being those of ref 5 at 100 and 700 Torr of N_2). The temperature dependence expression originally recommended by these authors was not a very good fit of their data and unfortunately (from an atmospheric modeling standpoint) this fit was poorest at the lowest temperatures. As a result, the most recent recommendation⁶ has coupled these experimental results with **RRKM** calculations⁷ to yield an equation which gives better agreement with the low-temperature data. This evaluation points out the need for further experimental studies, particularly at stratospheric temperatures and pressures in order to directly determine the temperature dependence of the low-pressure limit and thereby verify the recommended rate expression. It was for this explicit purpose that we undertook the present investigation using the flash photolysis UV absorption apparatus from our earlier work. Experiments were conducted at total pressures (M = N_2) of 25, 50, and 100 Torr over the temperature range 228-358 K employing pseudo-first-order kinetic conditions ([NO₂] \gg $[HO_2]_0$ with some minor corrections being made for the second-order removal of HO_2 via the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{2}$$

Experimental Section

The fabrication and use of our flash photolysis UV absorption apparatus have been described previously.^{2,8} As in these earlier room temperature experiments, HO₂ radicals were produced via the photolysis of reaction mixtures containing Cl₂, CH₃OH, O₂, and NO₂ according to the reaction sequence

 $Cl_{2} + h\nu \rightarrow 2Cl$ $Cl + CH_{3}OH \rightarrow CH_{2}OH + HCl$ $CH_{2}OH + O_{2} \rightarrow HO_{2} + CH_{2}O$

Concentrations of these compounds were chosen such that HO_2 production was complete within 10–20 μ s after the flash. The HO_2 radical absorption at 225 nm was followed with 3-nm resolution utilizing a multipass optical configuration (450-cm pathlength) employing a xenon arc lamp. As described in ref 2, care had to be taken to avoid NO production from NO₂ flash photolysis in order to minimize any contributions to the HO_2 decays from the rapid reaction

$$HO_2 + NO \rightarrow OH + NO_2$$
 (3)

To accomplish this, the flash photolysis wavelengths were limited by the Pyrex fabrication of the cell in conjunction with a $Cl_2/$ Br₂/BrCl equilibrium gas filter mixture admitted to a chamber between the flash lamp annulus and the reaction cell. By appropriate selection of filter-gas concentrations in our 298 K experiments, we were able to dramatically decrease the NO₂ photolysis above 340 nm with only a modest reduction in the Cl₂ photodissociation between 300 and 340 nm. The efficiency of this filter was not altered above room temperature (since the temperature dependence of the $Br_2 + Cl_2 \approx 2BrCl$ equilibrium constant is not very large). However, at temperatures below 298 K, the vapor pressure of Br_2 (and to a somewhat lesser extent, BrCl) drops off quite rapidly. As a result, for the lower temperature experiments, the filter mixture was adjusted to maximize the equilibrium concentrations of Br₂ and BrCl at their respective vapor pressures. At each temperature, the NO_2 photolysis through the filter was checked by monitoring NO_2 in absorption at 400 nm before and after multiple flashes. Further reduction in NO_2 photolysis was then achieved by lowering the flash lamp voltage (i.e., flash intensity). Experiments were finally performed under

conditions where (through the combination of filter transmission and flash lamp energy) NO_2 photolysis was less than 0.15% per flash, thus limiting kinetic contributions from reaction 3 at less than 10%.

An equally important consideration in the data analysis from these experiments is the level of a second-order component (due to reaction 2) in the pseudo-first-order HO₂ decays. This interference and its analytical resolution have been discussed fully in ref 2. Briefly, attempts were made to minimize such contributions by working at low initial concentrations of HO₂. However, when the corrections were required their magnitudes were determined from fits to computer data simulated by using similar initial radical concentrations and first-order decay rates. As before, these corrections were typically in the range of 5-10% with only the low [NO₂] runs at 25 Torr requiring as much as 20%.

The desired photolysis/reaction mixtures were prepared by combining calibrated flows of the appropriate gases in a mixing chamber immediately upstream of the reaction cell. This flowing procedure allowed for cell residence times ranging from ≤ 10 s at 25 Torr to ≈ 30 s at 100 Torr corresponding to complete sample replacement every 2–5 flashes. Experimental decay curves were typically the signal average of 100 flashes and were analyzed by a nonlinear least-squares fitting of the equation²

$$\ln (I_{\infty}/I) = (lC_0\sigma) \exp(-k^{1st}t)$$

for the determination of I_{∞} (the postflash, postreaction analysis light intensity), $lC_0\sigma$ (the product of the analysis path length, the initial radical concentration, and a composite absorption cross section), and k^{lst} (the pseudo-first-order decay rate). As discussed in our earlier publication,² this modified form of the first-order kinetic absorption equation is required to account for absorption of the analysis light by product HO₂NO₂ and reactant NO₂. The bimolecular rate constant at a particular total pressure was then determined from the slope of a plot of the corrected first-order decay rates vs. NO₂ concentration.

The temperature of the entire flash photolysis/reaction cell was controlled by the passage of water or ethanol (from an external temperature regulator) through a jacket surrounding the cell. The mixing chamber was also thermostatted by this same liquid flow in order to ensure complete temperature equilibration of the gas mixtures. The second-order rate constants were thus determined for all three N₂ pressures over the temperature range 228–358 K.

The ranges of concentrations for the various mixture components were (in units of molecules/cm³) as follows: Cl₂, (8–20) $\times 10^{16}$; CH₃OH, (2–10) $\times 10^{15}$; NO₂, (1–50) $\times 10^{14}$; and O₂, (1–3) $\times 10^{17}$. The desired total pressures were achieved through the addition of N₂. The variation in [Cl₂], coupled with changes in flash energy from 100 to 200 J, resulted in a range of [HO₂]₀ from 2 $\times 10^{13}$ to 6 $\times 10^{13}$ molecules/cm³. The reactant gasses used were of the following purities: Cl₂, 99.6% (used after redistillation); CH₃OH, Spectral Grade (used after vacuum drying and redistillation); NO₂, 99.5% minimum (redistilled and stored as a dilute mixture in O₂); O₂, 99.99%; and N₂, 99.999%.

The concentration of NO₂ at each temperature was limited to that level at which its dimerization to form N₂O₄ could cause significant depletion in the NO₂ concentration. The determinations of these values were made by using values for the dimerization equilibrium constant (K_p) calculated from the JANAF Thermochemical Tables.⁹ The potential for such complications was greatest at the lowest temperature (228 K) where K_p is calculated to be approximately 1.4×10^{-4} atm⁻¹ for the process

 $N_2O_4 \rightleftharpoons 2NO_2$

At this temperature the maximum NO₂ concentration used in the kinetic runs was 1×10^{15} molecules cm⁻³ and 15% dimerization is predicted. Since the rate constant at this temperature was calculated from the slope of a k^{1st} vs. concentration plot which

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Figure 1. Experimental HO₂ decay curve (dots) and computed first-order fit (solid line). Reaction conditions: T = 283 K, p = 100 Torr, [NO₂] = 34.8 mTorr, signal accumulation = 40 flashes, $k^{1st} = 740 \pm 50$ s⁻¹.



Figure 2. Plots of first-order decay rates vs. NO₂ partial pressure: (O) T = 263 K, p = 25 Torr; (X) T = 263 K, p = 100 Torr. The lines are the weighted least-squares fits.

included many experiments ranging in NO₂ concentration from 1×10^{14} to this maximum, the error in the rate constant would be expected to be considerably less than this 15%. This matter is taken into account in our later consideration of systematic errors.

Finally, the thermal decomposition of the product HO_2NO_2 at the highest temperatures used in this investigation was too slow to complicate the observed kinetics. Using the equilibrium constant data from ref 6, we calculate a lifetime at our highest temperature of more than 300 ms whereas HO_2 decays were followed on a time scale between one and two orders of magnitude shorter.

Results and Discussion

In Figure 1, a representative HO₂ absorption decay curve is shown along with the profile resulting from a nonlinear leastsquares first-order analysis of the data. The 15 to 1 signal to noise level does not represent the limits of sensitivity achievable in these experiments. Significant improvement in this ratio could have been achieved through greater signal averaging or by increasing the analysis path length. However, the data curve shown yielded a first-order fit with a 2σ error band of better than 7% and we used this lack of ambiguity in the kinetic interpretation as a guide to the conditions for data acquisition. First-order decay rates from approximately 500 such experiments were analyzed as a function of NO₂ concentration to yield second-order rate constants associated with the pressure and temperature of operation. For the k^{1st} vs. [NO₂] analyses, a weighted linear-least-squares procedure was used in order to prevent any biasing of the fits. In this procedure, each value of k^{1st} was weighted by the reciprocal of the square of its standard deviation. An example of these fitted data sets is shown in Figure 2 and a complete summary of the k₁ values determined in these experiments is presented in Table I. The error limits given in this table are two standard deviations from the statistical analysis and, as such, indicate the range of precision of the data. An assessment of all possible errors associated with these measurements (including the role of NO₂ di-

TABLE I: Rate Constants for Reaction 1 over the Temperature Range 228–358 K $\,$

	$k_1 \times 10^{13}, a, b \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
temp, K	p = 25 Torr	p = 50 Torr	p = 100 Torr
358	0.60 ± 0.09	1.02 ± 0.15	1.92 ± 0.25
337	0.81 ± 0.08	1.46 ± 0.11	2.37 ± 0.31
317	1.03 ± 0.09	1.97 ± 0.16	3.19 ± 0.32
298	1.21 ± 0.14	2.32 ± 0.56	3.49 ± 0.93
283	1.62 ± 0.11	2.80 ± 0.23	4.89 ± 0.50
263	2.39 ± 0.42	3.77 ± 0.55	6.69 ± 0.84
244	3.02 ± 0.63	4.55 ± 0.54	7.20 ± 1.32
228	3.65 ± 0.93	5.76 ± 1.64	8.46 ± 1.98

^a The results at 298 K are from ref 2. ^b The quoted uncertainties are the 2σ values from the weighted least-squares analysis.



Figure 3. Falloff curves at 298 K for (a) $M = N_2$ and (b) $M = O_2$. Experimental points: (O) ref 2; (X) ref 5. The solid lines are fits to the combined data sets as discussed in the text.

merization) results in our assignment of $\pm 30\%$ for 95% confidence limits.

As discussed in our earlier paper,² the room temperature data for reaction 1 can be represented by the Troe formulation³

$$k([M],T) = \{k_{0,M}(T)[M]/(1 + k_{0,M}(T)[M]/k_{\infty}(T))\}F_{c}^{1/\alpha}$$
(I)

where

$$\alpha = 1 + \{(1/N) \log (k_{0,M}(T)[M]/k_{\infty}(T))\}^2$$
$$N = 0.75 - 1.27 \log F_c$$

It was the goal of the present work to determine the temperature dependencies of $k_{0,M}$ and k_{∞} expressed as

$$k_{0,M}(T) = k_{0,M}(300 \text{K}) \{T/300\}^{-n}$$
 (II)

$$k_{\infty}(T) = k_{\infty}(300\text{K}) \{T/300\}^{-m}$$
 (III)

where the room temperature values of the falloff parameters could be determined from the eq I analysis of our earlier results. Although reaction 1 is in the falloff region between third- and second-order kinetics at pressures near 100 Torr, the temperature dependence exhibited by our data from 25 to 100 Torr has limited $k_{\infty}T$ -dependence characteristics. As a result, when our T-dependent data base was analyzed by using eq I-III with $k_{0,N_2}(300K)$ and $k_{\infty}(300K)$ taken from ref 2, the determination of *n* was quite precise while that for *m* was considerably less specific. We, therefore, decided to analyze our present data together with the 100- and 700-Torr N₂ data of Sander and Peterson.⁵ To maintain a consistency in the analysis, the composite room temperature N₂ and O₂ data from both laboratories^{2.5} were fit to eq I with F_c fixed⁶ at 0.6 yielding the room temperature falloff parameters (in molecular units)

$$k_{0,N_2}(300\text{K}) = 1.8 \times 10^{-31}$$

 $k_{0,O_2}(300\text{K}) = 1.5 \times 10^{-31}$
 $k_{\infty}(300\text{K}) = 4.7 \times 10^{-12}$



Figure 4. Dependence of k_1 on temperature at different pressures of N_2 . Experimental points: (O) this work at 25 Torr; (X) this work at 50 Torr; (*) this work at 100 Torr; (**a**) ref 5 at 100 Torr; (**b**) ref 5 at 700 Torr. The lines drawn at each pressure come from a fit of this complete data set to eq I-III.

The assignment of a fixed value for F_c does not precisely follow the Troe³ theory to the letter since F_c has a temperature dependence of its own, although calculations by Patrick and Golden⁷ indicate only a small change in F_c (from 0.72 to 0.61) for this reaction between 200 and 300 K. While the analysis performed in our room temperature studies demonstrated a significant dependence of k_{∞} on F_c , this dependence was greatest for F_c values below 0.5. In addition, only a small change in k_0 was observed for a nearly twofold variation in F_c . Thus, adoption of the 0.6 value for F_c chosen by the NASA Panel for Data Evaluation does not result in k_0 and k_{∞} values far removed from the "true" lowand high-pressure limiting rate constants.

The room temperature falloff curves for this composite data base are shown in Figure 3. With these values for $k_{0,N_2}(300K)$ and $k_{\infty}(300K)$, the temperature-dependent N₂ data from both laboratories were then fit to eq I-III by using a weighted nonlinear least-squares analysis. This treatment yielded

$$n = 3.2 \pm 0.4$$

 $m = 1.4 \pm 1.0$

where the uncertainties expressed are two standard deviations from the least-squares fit. Thus the temperature dependence of the falloff parameters can be expressed as

$$k_{0,N_2}(T) = 1.8 \times 10^{-31} \{T/300\}^{-(3.2\pm0.4)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_{\infty}(T) = 4.7 \times 10^{-12} \{T/300\}^{-(1.4 \pm 1.0)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The composite data set is shown with the computed curves in Figure 4. As can be seen there is excellent agreement between the 100 Torr data of the present study and that of ref 5 and the computed curves are not biased toward either end of the pressure or temperature ranges. The temperature dependencies determined are only moderately different from those currently recommended for atmospheric modeling⁶ which, as mentioned, are based on a limited data set coupled with theoretical computations. These differences are most evident in the low-pressure/high-temperature region and are not very significant under stratospheric conditions.

Acknowledgment. The research described in this manuscript was conducted at the National Bureau of Standards with the support of the National Aeronautics and Space Administration (Agreement W-15,816).

Registry No. HO₂, 3170-83-0; NO₂, 10102-44-0.

Kinetic Control in Two-Electron Homogeneous Redox Electrocatalysis. Reduction of Monohalobiphenyls

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Kinetic control of the two-electron electrocatalytic dehalogenation of monohalobiphenyls to biphenyl was elucidated by analyzing voltammetric data with expanded-grid digital simulation/nonlinear regression. The method involves comparing goodness of fit of limiting and mixed kinetic simulation models to the data and is applicable to second-order conditions. The rate-determining step in the dehalogenations was confirmed as electron transfer between the electrochemically generated phenanthridine anion radical and 4-chloro- (4-CB) and 4-bromobiphenyl (4-BB), rather than decomposition of the halobiphenyl anion radical. Rate constants for this step of $(1.42 \pm 0.12) \times 10^3$ M⁻¹ s⁻¹ for 4-CB and $(5.1 \pm 1.8) \times 10^4$ M⁻¹ s⁻¹ for 4-BB showed considerably improved precision (and accuracy in the latter case) over rate constants obtained under pseudo-first-order conditions, where the catalytic current had to be extracted from large currents for direct reduction of excess substrate. The simulation/regression method is general for two-electron homogeneous electrocatalytic reactions following similar mechanisms. Synthetic data were used to show that, for systems under mixed kinetic control, rate constants for both homogeneous electron transfer and decomposition of the haloaromatic anion radical can be estimated simultaneously.

Introduction

Reductive dehalogenation of mono- and polyhalobiphenyls (e.g., PCB's) in N,N-dimethylformamide (DMF) is catalyzed at mercury and glassy carbon electrodes by soluble organic redox couples¹⁻⁴ which accept electrons rapidly from the cathode. These

reactions are examples of homogeneous redox electrocatalysis, in which the electrochemically generated anion radicals of the catalyst transfer electrons to the PCB's, yielding biphenyl by a stepwise reduction of carbon-halogen bonds. These two-electron dehalogenations were studied for five halobiphenyl substrates and fifteen catalysts⁴ under conditions pseudo-first order in catalyst. Loss of the first halogen follows¹⁻⁴ Scheme I, similar to that for ha-

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