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Quenching Rate Constants for PCl($b^1\Sigma^+$, $v' = 0$)

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The reaction of metastable Ar($^3P_{0,2}$) atoms with PCl_3 has been developed as a source of metastable PCl($b^1\Sigma^+$) molecules in a flow reactor at 300 K. The total quenching rate constants were measured for 23 molecules, and they are in the 2×10^{-14} to 3×10^{-11} cm^3 molecule^{-1} s^{-1} range. An electronic-to-vibrational (E−V) energy-transfer mechanism is used to discuss the quenching of PCl($b^1\Sigma^+$), and the experimental rate constants are compared to similar data for PF($b^1\Sigma^+$), NF($b^1\Sigma^+$), and NCl($b^1\Sigma^+$) molecules. An influence of the type of halogen substituent in the reagent molecule on the quenching rate constants is identified, and a role for attractive molecular interactions needs to be added to the E−V model. The Ar($^3P_{0,2}$) + PCl_3 reaction gives vibrationally excited PCl($b^1\Sigma^+$) molecules and the $\Delta v = +1$ and $+2$ sequences were observed in addition to the $\Delta v = 0$ main sequence.

Introduction

The success of the singlet-oxygen iodine atom laser[1] has encouraged spectroscopic and kinetic studies of the energy storage and energy-transfer properties of singlet metastable states of molecules that are isovalent with O_2. The gas-phase quenching rate constants of O_2($b^1\Sigma^+$ and $a^1\Delta$)[2] and NF($a^1\Delta$ and $b^1\Sigma^+$)[3] already have been systematically studied. The PF, NCl, and PCl molecule have similar $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$ states,[4] and they continue to be the subject of active investigation.[5−8] The PCl($b^1\Sigma^+$) molecule has an energy of 1.5 eV and a radiative lifetime of ~4.9 ms.[6] The lifetime is sufficiently long that PCl(b) can be conveniently studied by the flow reactor technique.[6]

The reaction of Ar($^3P_{0,2}$) atoms with PCl_3 was used by Coxon and Wickrammaaratchi[9] as a source of PCl($A^3\Pi - X^3\Sigma^-$) emission, and they characterized the spectroscopy of the PCl(A and X) states. They also reported the formation of PCl($b^1\Sigma^+$) in the reaction. In this work, we have utilized the Ar($^3P_{0,2}$) + PCl_3 reaction as a convenient source of PCl(b) molecules for kinetic studies in a flow reactor. This source, which uses Ar carrier gas, complements the dc discharge through a flow of He/PCl_3 mixture that was used by Zhao and Setser.[6] The earlier study focused on measuring the PCl(b) radiative lifetime and studying the chemical reactions with molecular halogens. In the present work, we have extended the measurements of the reaction rate constants of PCl(b) to include 23 additional, mainly organic, molecules at 300 K.

The quenching rate constants for PCl(b) range from 3×10^{-11} to 2×10^{-14} cm^3 molecule^{-1} s^{-1}, and they are larger than for NCl(b), NF(b), or PF(b) with the same reagent. The relatively small rate constants, the dependence of the rate constants on vibrational energy defect, and the similarity to the results for NCl(b) and PF(b) suggest that the mechanism for quenching is usually electronic-to-vibrational (E−V) energy transfer with PCl($a^1\Delta$) being the product state. The model formulated by Schmidt[10] to correlate the E−V rate constants with the energy defect for the process is applied to the new PCl(b) data. However, the lack of knowledge for the energy difference between PCl(b) and PCl(a) makes quantitative comparison impossible. The quenching rate constants of PCl(b) and PF(b)[5] by the methyl and ethyl halides have a dependence on halogen substituent, and this trend cannot be explained by the nearly resonant E−V energy transfer model as formulated by Schmidt.

Experimental Techniques

The experimental apparatus employed for this work has been described previously.[11] It consists of a prereactor with discharge zone, the main flow reactor, the pumping system, and the monochromator with detection system. The discharge tube (2 cm diameter and 10 cm long) was connected to the main flow reactor (3 cm diameter) via a right angle bend to reduce the scattered light from the discharge. The metastable Ar($^3P_{0,2}$) atoms are generated by passing a flow of Ar through a hollow-cathode discharge.[12] The applied voltage for the discharge was approximately 400 V with a current of ~0.1 mA. The operating pressure was ~2.5 Torr for these experiments. Two liquid-N_2-cooled traps filled with molecular sieves were used to partially remove H_2O and CO_2 impurities before the Ar entered the hollow-cathode discharge. The main reactor was 70 cm in length; two reagent inlets were placed 3 and 13 cm downstream from where the Ar flow entered the reactor. The quenching reagents were added at the second inlet. The PCl_3 flow was added at the first reagent inlet. The emissions of the product fragments from the Ar($^3P_{0,2}$) + PCl_3 reaction were observed from the first window of the reactor. The PCl($b,v' = 0 \rightarrow X,v'' = 0$) emission intensity was observed at the second window in order to measure the relative PCl(b) concentration after a given reaction time.

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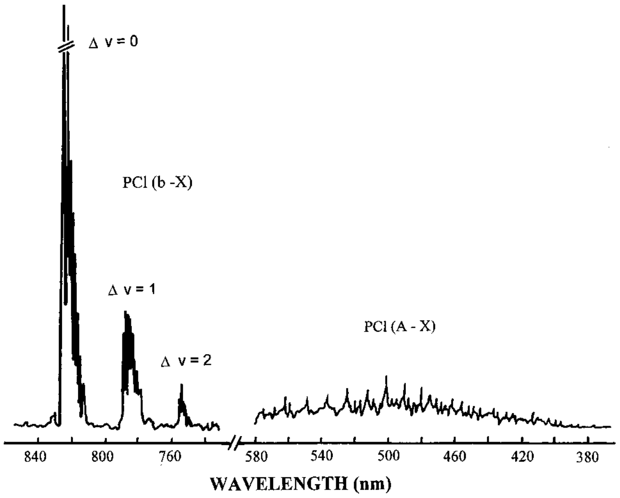

Figure 1. Overall emission spectrum from Ar($^3P_{0,2}$) + PCl_3 reaction observed at the first window of the reactor. The response was increased by a factor of 10 to record the PCl(b−X) emission spectrum. The spectrum has not been corrected for the variation of response of the detection system with wavelength. The response declines for longer wavelength.

The detection system consists of a 0.75 m monochromator fitted with a grating blazed at 430 nm, an RCA C31034 photomultiplier tube cooled to −30 °C, a photon counting system, and an $x-y$ recorder.

The PCl(b) concentration generated from the PCl_3 reaction is a significant (see next section) fraction of the Ar($^3P_{0,2}$) concentration, which places it in the low 10^9 molecule cm^{-3} range. Thus, the loss rate of the PCl(b) concentration will follow pseudo-first-order kinetics in the presence of added reagent. The competing first-order removal process, corresponding to radiative decay(τ^{-1}) and quenching by collisions at the wall (k_w), causes no difficulty providing that these terms are constant. The quenching rate constants of the PCl(b) molecules by the added reagents could be obtained from the plot of $\ln(I_0/I)$ vs [Q], as indicated by eq 1.

$$\ln(I_0/I) = (k_Q[Q] + \tau^{-1} + k_w)\Delta t \qquad (1)$$

I_0 is the intensity of PCl(b) emission before the quenching reagent is added. I is the intensity of PCl(b) present for a concentration [Q] of added reagent, k_Q is the quenching rate constant, and Δt is the reaction time. The flow speed was about 40 m/s, corresponding to a reaction time of ~8 ms. In the present work, the Pyrex glass reactor was not coated with wax to inhibit the loss from quenching at the wall.[6] The PCl(b) radiative lifetime is 4.9 ms, and, even if k_w is small, the loss of [PCl(b)] along the reactor is significant in the absence of added reagent. The concentration of PCl_3 added to the reactor was typically 5 × 10^{12} molecule cm^{-3}, which is too low to cause any quenching,[6] and the $k_{PCl_3}[PCl_3]$ term has been omitted from eq 1.

Experimental Results

1. Ar($^3P_{0,2}$) + PCl_3 Reaction as a Source of PCl($b^1\Sigma^+$) Molecules. The global emission spectrum (>350 nm), uncorrected for response of the detection system, from quenching of Ar($^3P_{0,2}$) atoms by PCl_3 is shown in Figure 1. Although nearly all of the metastable PCl(b) molecules flow out of the observation zone, the total PCl(b−X) emission intensity is still comparable to or higher than the emission intensity from the allowed PCl($A^3\Pi-X^3\Sigma^+$) transition.

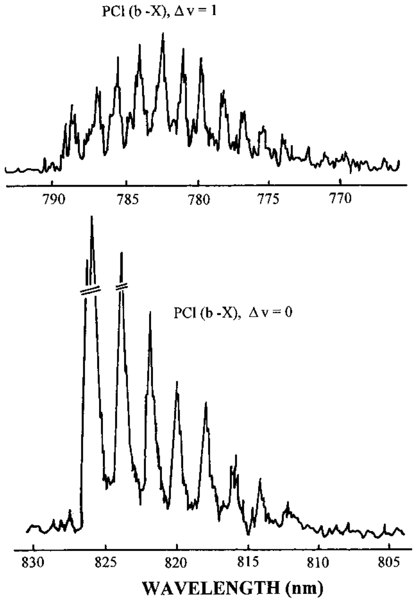

Figure 2. Emission spectrum of the PCl(b−X) transition showing resolved bands of the $\Delta v = 0$ and $\Delta v = 1$ sequence. The 0−0 and 1−1 bands are off the scale of this plot.

$$\begin{aligned} Ar(^3P_{0,2}) + PCl_3 &\rightarrow Ar + PCl_3^+ + e^- \\ &\rightarrow ArCl^* + PCl_2 \\ &\rightarrow PCl_3^* + Ar \end{aligned} \qquad (2)$$

The ionization and ArCl* formation steps have been studied previously,[13] and they have branching fractions of ~0.3 and ~0.03, respectively. The branching fraction for PCl($A^3\Pi$) formation[13] is ~0.01. Since PCl(b) is metastable, the emission intensity cannot be used easily to obtain a product branching fraction, but the formation of PCl(b) must be a significant pathway, based upon the observed intensity and comparison to similar experimental studies with NF(b) formed from Ar($^3P_{0,1}$) and NF_2.[3a] We estimate that PCl(b) formation from dissociation of PCl_3^* must correspond to >10% of the total quenching in reaction 2. The dissociation of PCl_3^* gives vibrationally excited PCl(b,v') molecules, as shown by the emission bands from high v' levels in the spectra of Figure 2. The $\Delta v = 0$ sequence extends to $v' = 7$, and the 10−9 band is evident in the +1 sequence (770−790 band). The lower resolution emission in Figure 1 also shows the presence of a weak $\Delta v = +2$ band. Since $r_e' \lesssim r_e''$ for the b−X transition, the $\Delta v = 0$ sequence dominates the spectrum; however, the Franck−Condon factors calculated[14] from RKR potentials and data in ref 15 suggest that the intensities of the $\Delta v = +1$ transitions will be comparable to the $\Delta v = 0$ transitions for $v' \geq 3$. Although the vibrational distribution is extended, the majority of the PCl(b) population is in the $v' = 0$ and 1 levels. The spectra shown in Figures 1 and 2 are fully consistent with the results of ref 9.

To use the Ar($^3P_{0,2}$) + PCl_3 reaction as a clean source for studies of the PCl(b) electronic quenching reaction rates, it is desirable to have a 300 K Boltzmann vibrational distribution for PCl(b). The desired vibrational relaxation was accomplished by adding excess PCl_3 at the first reagent inlet. When excess PCl_3 was added, the only observable PCl(b−X) emission at the first window was the 0−0 band at 826.1 nm. The addition of excess PCl_3 also ensured that all the Ar($^3P_{0,2}$) atoms had been

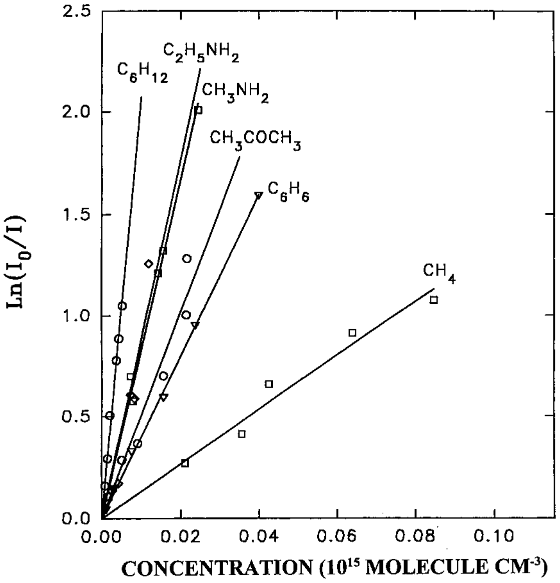

Figure 3. First-order quenching plots for PCl(b) by CH_4, C_6H_6, acetone, CH_3NH_2, $C_2H_5NH_2$, and *cyclo*-C_6H_6. The reaction time was 8 ms.

removed and that only the decay of the [PCl(b)] needed to be included in the rate law after the reagent was added to the reactor.

Experiments also were done in which PCl_3 was added to a flow of He(2^3S) metastable atoms. A weak PCl(b−X) emission could be observed. However, the Ar($^3P_{0,2}$) reaction gave more than an order of magnitude stronger signal, and reaction 2 is a much better source of PCl(b) molecules than the He(2^3S) + PCl_3 reaction. Zhao and Setser passed a mixture of PCl_3 in He through a dc discharge to generate adequate PCl(b) concentrations for subsequent kinetic measurement.[6] Direct comparison of the PCl(b) concentrations from reaction 2 vs the dc discharge in a PCl_3/He flow was not made in the same apparatus. Both PCl(b) sources are useful, and the choice mainly depends on whether He or Ar carrier gas is preferred. The Ar($^3P_{0,2}$) + PCl_3 system for the generation of PCl(b) is very similar to the Ar($^3P_{0,2}$) + NF_2 system for the generation of NF(b).[3a]

2. Quenching Rate Constants for PCl(b,$v' = 0$). The rate constants were measured using the fixed-point observation method, and the PCl(b,$v' = 0$) emission intensity was used to monitor the relative PCl(b) concentration. Sufficient PCl_3 was added at the first inlet to remove all the Ar($^3P_{0,2}$) atoms and to cause vibrational relaxation of the PCl(b) molecules. The reagent flow was added at the second inlet, and the decline in PCl(b) emission intensity was observed at the last window. Plots for the ratio of ln(I_0/I) vs reagent concentration are linear, as shown in Figures 3−5. Since the quenching rates are relatively slow, the reagents were metered to the reactor as pure materials, i.e., without preparation of dilute mixtures in Ar. The flow rates of the reagents were measured directly by switching the flow to a reservoir with a calibrated volume and recording the rise of pressure.

The plots of ln(I_0/I) vs [Q] always appeared to be linear, and the standard deviations of the slopes were about ±5%. To obtain rate constants from the slopes, the flow distance must be covered to a reaction time. This requires the total Ar flow rate, the pressure in the reactor, and utilization of the parabolic flow analysis, which includes the assumption that PCl(b) is quenched at the flow tube walls. The Ar flow rates were measured with a rotameter that was calibrated to a measured pressure rise in a large volume. The greatest uncertainty in the rate constant measurements is the conversion of the flow reactor distance to time. As a check on the method, a comparison was made to the rate constants for CH_4 and CO_2 that have been reported by other groups. The results from the present study using the parabolic flow relation, e.g., the plug flow time modified by the 0.6 factor to obtain Δt, gave the same rate constants as previously reported for CCl_4 and CO_2 (see Table 1). On the basis of the uncertainty in converting distance to reaction time, we assigned absolute uncertainties to the rate constants given in Table 1 to be ±25%, although the relative values within the measured set, which are governed by the reliability of the reagent flow rates, should be considerably better.

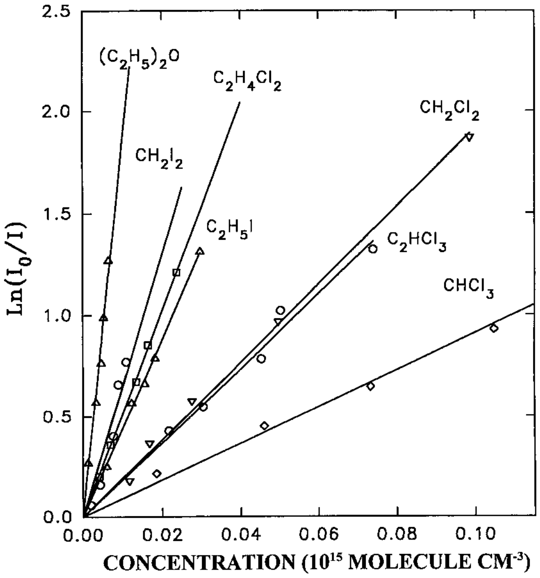

Figure 4. First-order quenching plots for PCl(b) by $CHCl_3$, C_2HCl_3, CH_2Cl_2, C_2H_5I, $C_2H_4Cl_2$, CH_2I_2, and $(C_2H_5)_2O$. The reaction time was 8 ms.

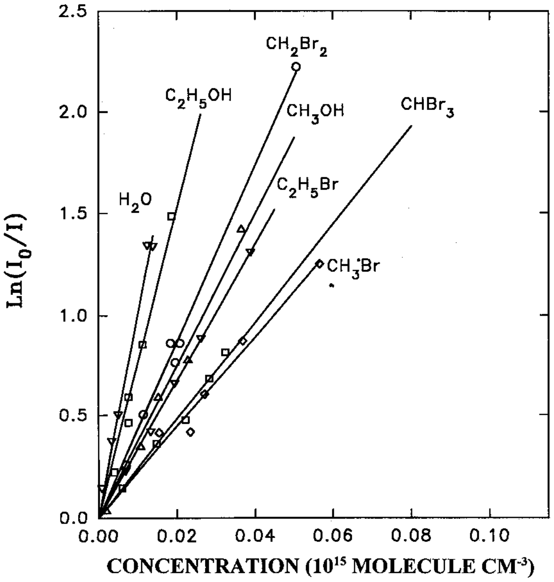

Figure 5. First-order quenching plots for PCl(b) by CH_3Br, $CHBr_3$, C_2H_5Br, CH_3OH, CH_2Br_2, C_2H_5OH, and H_2O. The reaction time was 8 ms.

The rate constants for CO, O_2, and CO_2 are $\leq 0.2 \times 10^{-13}$ and those for SO_2, $SOCl_2$, and $H_2(D_2)$ are $(1-4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The large kinetic isotope effect (a factor of 2.6) observed for H_2 and D_2 is typical for an E−V transfer mechanism.[3,5,6] The very small rate constant for O_2 is consistent with the endoergic (1020 cm^{-1}) nature of the energy exchange to give O_2(b) and a slow chemical reaction rate at 300 K. The rate constant for quenching of PCl(b) by PCl_3 was not explicitly

TABLE 1: Quenching Rate Constants (10^{-13} cm^3 molecule^{-1} s^{-1}) for PCl(b), NF(b), NCl(b), and PF(b)

reagent	PCl(b)[a]	NCl(b)[b]	NF(b)[c]	PF(b)[d]
CO	0.004	<0.01	0.02	0.10
D_2	1.7[e]	0.8	0.03	3.6
H_2	4.5[e]	2.0	0.25	0.40
HCl	25[b]	7.0	0.18	0.90
O_2	<0.01[b]	10	0.24	210.
CO_2	0.20 (0.20[e])		0.015	0.15
SO_2	1.9		0.010	
$SOCl_2$	1.1			
H_2O	160	62	8.6	2.8
CH_3OH	60	65	6.8	14
C_2H_5OH	120			
CH_3NH_2	130	37	3.7	61
$C_2H_5NH_2$	140			
CH_4	21 (19,[b] 20[e])	5.8	1.6	5.5
C_2H_6	45[b]	23	1.4	7.4
C_6H_6	64			
cyclo-C_6H_{12}	330			
CH_3Cl		15	2.1	5.3
CH_2Cl_2	31		1.5	
$CHCl_3$	15	5.9	0.64	1.2
$C_2H_4Cl_2$	82[f]	−30[f]		
C_2HCl_3	29			
CH_3Br	36	12	1.9	8.6
CH_2Br_2	70		2.1	
$CHBr_3$	36			2.5
C_2H_5Br	61	33		9.1
CH_3I		17	3.6	15.2
CH_2I_2	110			
C_2H_5I	70			
$(C_2H_5)_2O$	300			
CH_3COCH_3	73			2.6

[a] This work unless indicated otherwise. The uncertainty in the relative rate constants measured in this work should be ±10%. The absolute uncertainty should be better than ±25%; see text. [b] Taken from ref 6. [c] Taken from ref 3a. [d] Taken from ref 5. [e] Taken from ref 4. [f] The $C_2H_4Cl_2$ result can be compared to $k_Q = 30 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} measured[6] for NCl(b) with C_2H_5Cl.

studied. However, no quenching was observed in ref 6 or in this work for concentrations of 5×10^{12} molecules cm^{-3}, which gives a limit of less than 50×10^{-13} cm^3 molecule^{-1} s^{-1}; the true value for the rate constant is probably much less and comparable to that for $SOCl_2$.

The quenching rate constants for HCl, H_2O, and the organic molecules are all much larger than for the molecules mentioned above, and they are in the $(15-300) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} range. The number of C−H, O−H, or N−H bonds in a given molecule clearly affects the magnitude of the quenching rate constant. For example, the rate constants for the CH_4, C_2H_6, and *cyclo*-C_6H_{12} series increase systematically and $k_{CH_2Cl_2}/k_{CHCl_3}$ and $k_{CH_2}/k_{CHBr_3} \cong 2$. The smaller k_{CH_3Br} vs $k_{CH_2Br_2}$ may be related to the larger polarizability of CH_2Br_2, vide infra. If CH_2Br_2, $CHBr_3$, C_2HCl_3, and CH_2I_2 are excluded, because their rate constants are anomalously high, the average quenching rate constant per C−H bond for the molecules in Table 1 is $(15 \pm 5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}; the higher range of values usually correlates with those molecules with permanent dipole moments. If this average value is used for the C−H bonds of the alcohols, the rate constant associated with the OH bond (k_{OH}) is 80, 45, and 15×10^{-13} cm^3 molecule^{-1} s^{-1} for H_2O, C_2H_5OH, and CH_3OH, respectively. If a lower average k_{CH} value based on CH_4 and C_2H_6 is selected, the k_{OH} from CH_3OH would increase to $\sim 40 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Based on CH_3NH_2 and $C_2H_5NH_2$, the average k_{NH} value would be $\sim 40 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. It seems evident that the average quenching rate constant of PCl(b) associated with a NH or OH bond is larger than for a CH bond. The average quenching rate constants associated with the C−H, O−H, and N−H bonds for PCl(b) seem to be a factor of 2−4 larger than for NCl(b), and the rate constants for both usually are larger than for NF(b) or for PF(b). In summary, the results in Table 1 show that PCl(b) always has the largest rate constant of the four cases for a given reagent molecule.

In addition to a general dependence on the number of C−H bonds in a molecule, the rate constants for CH_2Cl_2, CH_2Br_2, and CH_2I_2 show a dependence on halogen, increasing from 31, 70, and 110×10^{-12} cm^3 molecule^{-1} s^{-1} in the series. A similar trend exists for $CHCl_3$ vs $CHBr_3$ and for C_2H_5Br vs C_2H_5I. A dependence on halogen substituent also was found for quenching of PF(b) by CH_3X (X = F, Cl, Br, I),[5] but this dependence was much weaker for both NCl(b) and NF(b).[3,6] The increased polarizability of the heavier halogen atoms apparently causes stronger intermolecular interaction between PCl(b) and Q, which aids the quenching process. We suspect that the intermolecular interactions act to enhance the rates of the E−V mechanism discussed below, but interactions leading to chemical reaction cannot be excluded without product yield data.

Discussion

The magnitude of the quenching rate constants and the analogy to the PF(b), NF(b), and NCl(b) data strongly suggest that the quenching mechanism for PCl(b) is E−V transfer with formation of a vibrationally excited molecule, Q*, and PCl(a), e.g.,

$$\mathrm{PCl}(b^1\Sigma^+) + \mathrm{CH_4} \rightarrow \mathrm{PCl}(a^1\Delta) + \mathrm{CH_4}^* \qquad (3)$$

Schmidt has formulated a model for E−V transfer that has been successful in correlating the quenching rate constants for $O_2(a)$, $O_2(b)$, NF(b), and PF(b) with the energy defects of the excited reagent molecule. To apply the model to obtain rate constants, it is necessary to know the energy difference between the PCl(b) and PCl(a) states, which is not experimentally known. An estimate can be obtained from Zabel and co-workers' observation that the a−X energy is usually 0.55 of the b−X energy separation.[4] This estimate gives 5440 cm^{-1} for the energy different between the PCl(b−a) states. However, the ratios are 0.53 for PF and 0.62 for NCl, which correspond to an energy separation between PCl(b−a) of 5668 and 4599 cm^{-1}, respectively. The recent ab initio calculations[15] of the energy differences for the PCl(b,a,X) states give $\Delta E(b-a) = 2613$ cm^{-1}. However, the same calculation for NCl gave an energy difference of 4153 cm^{-1} vs the true value of 5759 cm^{-1}. Even if in error, the calculations suggest that PCl may resemble NCl more than PF, and perhaps the ΔE(b−a) value is less than 5000 cm^{-1}. The lack of a precise energy difference makes it impossible to make numerical comparisons with Schmidt's model because the final vibrational energy states of Q* cannot be even estimated. However, a summary of the qualitative aspects is still worthwhile.

According to Schmidt's model[10] the E−V quenching constant is given by eq 4:

$$k_Q = \sum_i k_i = C \sum_i \sum_{m,n} F_m F_n' R^i_{mn} \qquad (4)$$

Each terminal bond in the molecule has a rate constant k_i, which depends on the $F_m F_n' R^i_{mn}$ terms describing the energy transfer from ($b, v' = 0 \rightarrow a, v'' = m$) to the product molecule ($Q^*, v' = n \leftarrow Q, v'' = 0$). The F_m and F_n' terms are the Franck−Condon factors for the (b,0−a,m) transition and the stretching mode vibrational excitation, respectively. The R^i_{mn} term accounts for the energy defect for excitation of each bond, i, in the form of an exponential gap law, $\exp(-\alpha E^i_{mn})$ when $E^i_{mn} > 0$. The model has been fitted to rate constant data for O_2(b), NF(b), and PF(b), and the overall level of agreement is surprisingly good, even with the same values for the C ($(2-3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) and α (0.0032 (cm^{-1})$^{-1}$) parameters. The Franck−Condon factors for the ($b,0-a,m \neq 0$) transitions are quite small, and only the $m = 0$ transition need be considered for reactions with large rate constants. The largest rate constants for quenching of O_2(b), NF(b), and PF(b) correspond to nearly resonant energy transfer to two quanta of stretching vibrational excitation of O−H, C−H, and N−H bonds.[5,6] The model does not make any allowance for bending mode excitation, although for off-resonance cases, the data[5] suggest that stretch−bend combination product states[16] probably are important. The largest possible quenching rate constants for resonant energy transfer with $n = 2$ are about 5×10^{-13} cm^3 molecule^{-1} s^{-1} per terminal bond for the values of C and α quoted previously. Several rate constants for PCl(b) actually seem larger than this limit. Furthermore, the available electronic energy probably is less than the energy needed for 2 quanta of excitation for OH and N−H bonds, and perhaps for C−H bonds too, and a Boltzmann factor needs to be added to eq 4 to account for the endoergic nature of the process.[10]

Within the context of the Schmidt model, the larger rate constants for PCl(b) vs NCl(b) with H−Cl, C−H, O−H, and N−H bonds can be explained in two ways. If the E(b) − E(a) value is close to 5440 cm^{-1}, the values for C and/or α in eq 4 must be changed and the pleasing universal nature of the Schmidt model found for O_2(b), NF(b), and PF(b) is lost. The second possibility is that E(b) − E(a) is considerably smaller, perhaps in the 4500 cm^{-1} range. Then the final vibrational states would correspond to $\Delta v = 1$ excitation (or $\Delta v = 1$ plus bending excitation) and the F_n' term would be a factor of ca. 25 larger than for $\Delta v = 2$ excitation. Experimental measurement of E(PCl(a)) is required before further discussion is warranted.

Even if E(b) − E(a) was known, the Schmidt model cannot explain the systematic increase in k_Q for the methyl halides as Cl is replaced by Br and I atoms. A similar trend with halogen substituent exists for the PF(b) quenching data, but not for NCl(b) or NF(b). The possibility for greater attractive interaction between PF(b) and Q vs NF(b) and Q was discussed when the PF(b) results were presented.[5] The recent ab initio calculations[15] predict a smaller dipole moment for PCl(b) than NCl(b), and the previous suggestion for the role of a larger dipole moment for PCl(b) and PF(b) may not to be an acceptable explanation for the larger intermolecular interaction for the PF(b) and PCl(b) reactions. The rate constants for PF(b) and PCl(b) do scale with the polarizability of Q for the same class of reagent, i.e., the CH_3X or C_2H_5X series. Adding a term of the form $\exp(\beta\alpha_Q)$, where α_Q is the polarizability of the reagent, to eq 4 with assignment of a new constant C' to eq 4 can provide better fits to the PF(b) and PCl(b) data. However, the model now has three parameters, C', α, and β, and the physical significance of the added polarizability term is questionable. The bond energies for the PCl−X and PF−X radicals are sufficiently uncertain[5,15,17] that quenching by chemical reaction cannot be excluded and experimental verification of physical quenching vs chemical reaction is needed for proof of the mechanism. It should be noted, however, that the large kinetic-isotope effect observed for quenching of PF(b) by $CHCl_3$ and $CDCl_3$ supports an E−V mechanism.

Conclusions

A clean source of PCl($b^1\Sigma^+$) metastable molecules for experiments in flow reactors has been developed that is based on the Ar($^3P_{0,2}$) + PCl_3 reaction. This source is suitable for kinetic studies using the PCl(b−X) spontaneous emission to monitor the relative [PCl(b)]. This source also could be used to probe for spectroscopic transitions to higher energy singlet states of the PCl molecule. Electronic quenching rate constants were measured at 300 K for 23 reagent molecules. For a given reagent, the quenching rate constants for PCl(b) are the largest of the PF(b), NF(b), NCl(b), PCl(b) group. Although the quenching mechanism probably is E−V transfer, the energy difference between the PCl(b) and PCl(a) states is needed before the model can be discussed in further detail.

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References and Notes

(1) (a) McDermott, W. E.; Pchelkin, N. R.; Benard, D. J.; Bousek, R. R. *Appl. Phys. Lett.* **1978**, *32*, 469. (b) Benard, D. J.; Medermott, W. E.; Pchelkin, N. R.; Bousek, R. R. *Appl. Phys. Lett.* **1979**, *34*, 40. (c) Bachar, J.; Rosenwaks, S. *Appl. Phys. Lett.* **1982**, *41*, 18. (d) American Physical Society Study Group. *Rev. Mod. Phys.* **1987**, *59*, 541.

(2) Wayne, R. P. In *Singlet O_2*; Frimer. A. A., Ed.; CRC Press, Boca Raton, FL, 1985.

(3) (a) Cha, H.; Setser, D. W. *J. Phys. Chem.* **1989**, *93*, 255. (b) Du, K.-Y.; Setser, D. W. *J. Phys. Chem.* **1991**, *95*, 9352.

(4) Beielefeld, M.; Elfens, G.; Fink, E. H.; Kruse, N.; Wildt, J. K.; Winter, R.; Zabel, F. *J. Photochem.* **1984**, *25*, 419.

(5) Zhao, Y.; Setser, D. W. *J. Phys. Chem.* **1994**, *98*, 9723; **1995**, *99*, 1217.

(6) Zhao, Y.; Setser, D. W. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2979.

(7) (a) Ray, A. J.; Coombe, R. D. *J. Phys. Chem.* **1995**, *99*, 7849; **1993**, *97*, 3475. (b) Schwenz, R. W.; Gilbert, J. V.; Coombe, R. D. *Chem. Phys. Lett.* **1993**, *207*, 526.

(8) (a) Benard, D. J.; Boehmer, E.; Michels, H. H.; Montgomery, J. A., Jr. *J. Phys. Chem.* **1994**, *98*, 8952. (b) Benard, D. J.; Chowdhury, M. A.; Winker, B. K.; Seder, T. A.; Michels, H. H. *J. Phys. Chem.* **1990**, *94*, 7507. (c) Benard, D. J. *J. Phys. Chem.* **1996**, *100*, 8316.

(9) Coxon, J. A.; Wickrammaaratchi, M. A. *J. Mol. Spectrosc.* **1977**, *68*, 372.

(10) (a) Schmidt, R.; Afshari, E. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 788. (b) Schmidt, R. *J. Phys. Chem.* **1993**, *97*, 3658.

(11) Guo, J.-Z.; Gu, Y.-S.; Liu, C.-P. *Chem. Phys. Lett.* **1990**, *169*, 432.

(12) Sobcyznski, R.; Setser, D. W. *J. Chem. Phys.* **1991**, *95*, 3310. This reference describes various configurations for discharges that can be used to generate Ar($^3P_{0,\,2}$) atoms.

(13) Sadeghi, N.; Cheaib, M.; Setser, D. W. *J. Chem. Phys.* **1989**, *90*, 219.

(14) The Franck−Condon factor calculations were done with $r_e' = 1.993$ Å and $r_e'' = 2.015$ Å; see ref 15.

(15) Papakondylis, A.; Mavridis, A.; Metropoulos, A. *J. Phys. Chem.* **1995**, *99*, 10759.

(16) Boyankin, O. V.; Rizzo, T. R. *J. Chem. Phys.* **1996**, *105*, 6285. This paper, and many others, provide information on the intrinsic stretch−bend mode mixing for the C−H chromophore of CX_3H molecules.

(17) Latifzaden, L.; Balasubramanian, K. *Chem. Phys. Lett.* **1995**, *243*, 243.