calculations on δ-N_2. We are also indebted to J. M. Neff for patiently typing the manuscript, especially the correlation diagrams. S.B. expresses appreciation for a Graduate Research Assistantship sponsored by the Los Alamos National Laboratory's Center for Materials Science. This work was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences.

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Supplementary Material Available: An Appendix to this paper, giving correlation tables for all of the cubic and rhombohedral space groups listed in Table I, as well as the centrosymmetric tetragonal and orthorhombic structures, is available (33 pages). Ordering information is available on any current masthead page.

Flash Photolysis of Transient Radicals. 1. X_2^- with X = Cl, Br, I, and SCN[†]

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The radicals Cl_2^-, Br_2^-, I_2^-, and $(SCN)_2^-$ were prepared by photolysis of appropriate chemical systems with one laser and were subsequently photolyzed with a second laser. The first three species were photolyzed at 355 nm, and $(SCN)_2^-$ was photolyzed at 532 nm; I_2^- was also photolyzed at 700 nm. In each case, dissociation into the fragments X and X^- was detected by a bleach in the absorption of X_2^-. The quantum yield for this process is about 0.1 except for Cl_2^- where the value is 0.2. In no case was electron photodetachment observed. Observation of the recovery of the original absorption allowed the corresponding rate constant to be measured. The values for Cl + Cl^- (8×10^9 M^{-1} s^{-1}) and SCN + SCN^- (9×10^9 M^{-1} s^{-1}) have not previously been measured directly. In the case of Cl_2^- the bleach in absorption does not completely recover and the loss of absorption is dose dependent. Because the presence of acid allows a more complete recovery, it can be concluded that the product Cl atom is photolyzed by a second photon to produce OH and Cl^-. The quantum yield was determined to be about 0.5. This photoreaction is direct experimental evidence that the absorption band of Cl involves charge transfer from solvent. Detailed analysis of the bleaching and recovery behavior at high Cl^- concentrations showed no time lag which could be attributed to the $^2P_{1/2}$ Cl atom, implying a short lifetime for this species.

Introduction

There exist a number of techniques for investigating the properties and reactivity of stable molecules in the liquid phase which have not been applied widely to transient species such as radicals. One such technique is laser flash photolysis. The experimental setup needed is very similar to existing laser photolysis systems with the important addition of a second laser to photolyze the transient species. We have undertaken a program to investigate the photophysics and photochemistry of transient radicals in solution by time-resolved optical absorption spectroscopy. For a start, systems of the type X_2^- in aqueous solution (where X = I, Br, Cl, and SCN) have been studied. These systems have strong absorptions in the near-UV or visible regions, are structurally simple, and should have easily interpretable photophysics or photochemistry. One would like to know if resonant excitation of these species in solution would lead to either dissociation

$$X_2^- \rightarrow X + X^- \qquad (1)$$

or photodetachment

$$X_2^- \rightarrow X_2 + e^- \qquad (2)$$

The absorption maxima in water for the first three species[1] are similar to but slightly shifted from those in the gas phase[2] and halide crystals,[3] and the bands are also slightly broadened. The absorption spectrum of $(SCN)_2^-$[4] in other than the solution phase has not been reported. In fact, its existence in the gas phase is not known. From experiments[2a,c,d] and theoretical calculations,[5] all the excited states of X_2^- are known to be dissociative ($(SCN)_2^-$ excluded). For Cl_2^- in the gas phase, the efficiency of path 2 was found to be nonzero but less than 5%. Lee et al.[2d] concluded that negligible photodetachment would occur since the vertical ionization potential from their potential curves is 4.0 eV and greater than the photon energy at the peak of the absorption (3.65 eV). The electron affinity values are in the order $Cl_2 > Br_2 > I_2$ so that the photodetachment efficiency could be larger for Br_2^- and I_2^- than for Cl_2^-. In any case, the gas-phase behavior cannot be expected to hold exactly for the aqueous phase where there may be shifts and/or distortions in the potential energy curves for the ionic and neutral species in addition to extensive solvation of the ions. Resonance-enhanced Raman spectroscopy of Cl_2^-, Br_2^-, and I_2^- in solution[6] finds vibrational frequencies and anharmonicity values in reasonable accord with values based on theoretical potential curves for the gas phase. However, the dissociation of X_2^- species under equilibrium conditions in water is known to occur[1] with an equilibrium constant of about 10^{-5} M. Thus, it is likely that the adiabatic difference in energy of X_2^- relative to X and X^- in solution is less than implied by the gas-phase potential curves. The Raman experiment appears to sample the potential curve without solvent rearrangement.

The gas-phase potential energy curves for Cl_2^- are given in Figure 1. The curves for Br_2^- and I_2^- are similar but with larger separations between the $^2P_{1/2}$ and $^2P_{3/2}$ states of the atoms. Nothing is known about $(SCN)_2^-$, but because of the pseudohalogen nature of SCN, one might expect a general behavior that is very similar to that of the other halogen species. In this case, excitation to a bound state and consequent relaxation are also possible.

In addition to these points, photolysis of X_2^-—and particularly of I_2^-—would be an extension in a different direction of the

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[†] This is Document No. NDRL-2589 from the Notre Dame Radiation Laboratory.

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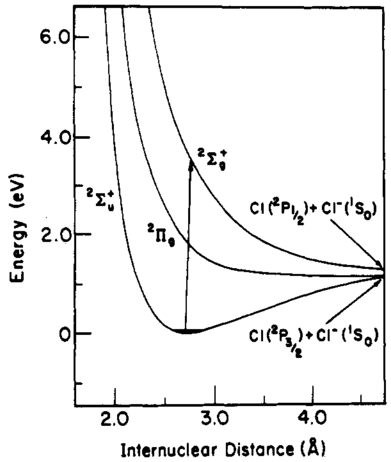

Figure 1. Potential energy curves for the ground and excited states of Cl_2^-—adopted from ref 5c and modified to include spin–orbit splitting of Cl. Only those excited states to which transition from the ground state is allowed are shown. The arrow indicates the transition corresponding to 355-nm excitation.

photolysis of I_2 in solution where the processes following photon absorption are still not well understood despite the tremendous amount of literature that already exists on this topic.[7] Even though our experiments are confined to the time scale of tens of nanoseconds, they form a basis for future experiments with picosecond resolution. In all cases, only dissociation (process 1) has been found. As a side benefit, the rate constants for the reaction

$$X + X^- \rightarrow X_2^- \tag{3}$$

have been determined directly. These data are very useful in unraveling the kinetic details of the formation of X_2^- in pulse radiolysis. As will be made clear below, Cl_2^- hapens to be a very special case under our experimental conditions in that the Cl atom produced also absorbs a photon and undergoes reaction.

Experimental Section

Sodium chloride (Fisher), potassium bromide (Mallinckrodt), potassium iodide (Fisher), sodium persulfate (Sigma), and potassium thiocyanate (Fisher) were used as received. The radicals were initially produced by a pulse of light at 248 nm from a KrF excimer laser (Tachisto 150XR). Iodide was photolyzed directly, and the other anions were oxidized by SO_4^- produced from $S_2O_8^{2-}$ by this laser. The subsequent photolysis 1–5 μs later was with the 355-nm third harmonic from a Quanta Ray DCR-1 YAG laser. (With I_2^- a second experiment was done with the output from a dye laser pumped by the second harmonic of the YAG laser.) In order to provide better time resolution in the case of Cl_2^-, additional experiments were carried out using a PRA LN-1000 nitrogen laser (337 nm) for the second photolysis. This laser has a 0.8-ns pulse width and 1.5-mJ pulse energy. Because of the large time jitter with this laser (~6 μs), it was necessary to provide a coincidence circuit so that data could be accepted only from those pulses in the correct time window.

To get good signals, it is necessary that the two lasers and the analyzing light all pass through the same part of the cell. The best approach was as shown in Figure 2. The initial radicals are formed by the laser beam traveling opposite to the analyzing beam. If the laser beam is of larger cross section than the analyzing beam, then the optical density will be measured correctly. The second laser beam is at 90° to the first. As long as the optical density of the transient at this wavelength is not too large, the changes recorded by the analyzing beam will be accurately measured. Apertures were provided to prevent the second laser beam from hitting any cell surface in direct view of the monochromator so that scattered light and fluorescence of the cell were avoided as much as possible. A narrow band interference filter was also used in front of the monochromator to further reduce scattered light. With these precautions, no change in optical density was observed when the second laser alone was used with the sample and only a very small amount of fluorescence or scattered light was seen. Only with the most sensitive experiments on Cl_2^- was it necessary to subtract traces taken without the first laser from data with both lasers firing. The cell was made of low-fluorescence silica, 5 × 5 mm inside dimension, and connected so that the solution could flow up through the cell. Typical flow rates were 5 cm^3 min^{-1}. Quantum yield measurements at 355 nm were made by comparing the observed bleach signal in each system with the absorbance of benzophenone triplet in benzene using the same pulse energy and without changing the position of the cell or optical components. The optical densities at 355 nm were taken into account in calculating the fraction of light absorbed. The quantum yield measurements at 532 nm made use of the triplet of tris(2,2′-bipyridyl)ruthenium chloride. Relative dose measurements were made by splitting off a fraction of the beam with a quartz plate and directing this light to a pyroelectric monitor.

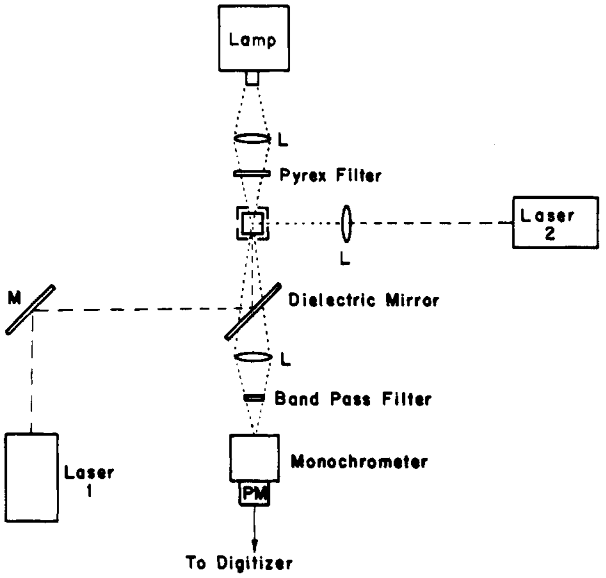

Figure 2. Photolysis arrangement used in these experiments. Laser 1 is at 248 nm and laser 2 at 355 nm or other wavelengths. The two mirrors for 248 nm have dielectric coatings and were optimized for 45° incidence. At the wavelength used for analysis the one mirror passes most of the analyzing light.

Time-resolved absorption measurements were made with an updated version of the apparatus described previously.[8] The analyzing light comes from a 1000-W xenon high-pressure lamp which is pulsed for 2 ms to increase the intensity. The photomultiplier signal passes through a circuit to back off the signal corresponding to the initial 100% transmission of the sample and then to a Tektronix R-7912 transient digitizer. For the experiment with the N_2 laser, a Tektronix 7912 AD digitizer with 7A29 preamplifier was used to provide the fastest possible response. The time constant of photomultiplier and digitizer together was about 1.5 ns. In this application, the digitizer was triggered from the laser pulse by means of a photodiode to reduce the jitter. The digital data are transferred to an LSI-11/2 microcomputer which controls the experiment, provides for averaging a number of transient responses, and processes the data to give optical density. The data are then transferred to a PDP 11/55 system for storage and further on-line analysis. The computer operates shutters in both analyzing and laser light beams. The time delays between the two laser pulses and the triggering of the digitizer are controlled by digital time delay boards from Evans Associates. For the present study, it is desirable to have a kinetic curve which represents the difference between the absorption by the radical formed

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[8] Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146.

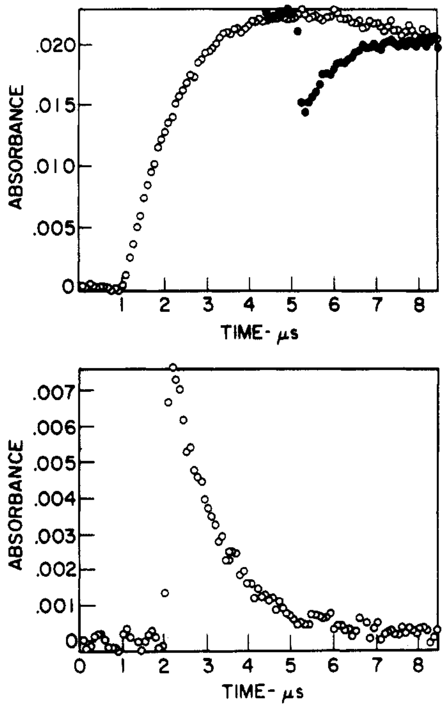

Figure 3. Top: Absorption profiles at 380 nm corresponding to 248-nm excitation alone (open circles) and to 248- and 355-nm excitation (closed circles) of 0.2 mM KI (average of 4 shots each). Bottom: The difference between the two signals above, obtained directly by the computer (as described in the text) and inverted for presentation, gives the bleach signal (15 shots). The digitizer was triggered at a later time so the time origin is offset.

by the first laser alone and that after the second photolysis. This difference is obtained by treating the signal in the absence of the second laser as the base line and using a base line subtraction option so that the computer takes the difference directly. The upper part of Figure 3 shows data taken with and without the second laser pulse. The bleach is seen to be about 30%. The difference between the two traces by using the procedure described above is shown in the lower part of the figure. In this mode, the calculation of optical density is not carried out correctly since the absorption produced by the first laser pulse is not taken into account. At the absorbance levels used, the conversion of percent transmission into optical density is sufficiently linear that no significant effect on the rate of recombination would occur. However, only data corrected for true I_0 values were used for quantitative yield calculations.

Results and Discussion

I_2^- and Br_2^-. A prime consideration in these studies is the fate of both fragments created by either the initial or subsequent photolysis. In the case of I^-, initial photoysis produces e_{aq}^- and I and it is necessary to dispose of the hydrated electron. If the solution is saturated with N_2O, the e_{aq}^- will be converted to OH which will produce another I_2^-. Since the subsequent photolysis of I_2^- happens only after the initial reactions are complete, any intermediates such as IOH^- are of no direct concern as long as they are converted to I_2^-. The I_2^- was photolyzed at 355 nm, and the absorption was monitored at the maximum of the UV band at 380 nm. An initial "bleach" was seen with a subsequent recovery. The recovery is a single exponential and is complete (see Figure 3, bottom). The fact that the bleach recovers completely means that there cannot be any other processes on the nanosecond time scale. A plot of rate constant for recovery vs. concentration of I^- is a straight line passing through the origin, whose slope must correspond to the rate constant for the recombination process. The rate constant so determined is 1.1×10^{10} M^{-1} s^{-1} in agreement with previous results.[9] The quantum yield for dissociation (0.12) and the rate constant for reaction 3 are listed in Table I. The extinction coefficients used in this measurement are given in Table II. Similar results were obtained for excitation at 700 nm so that excitation in either band leads to dissociation, even though the excited states are different for the two bands. When the solution is saturated with pure N_2O, the electron lifetime is too short to allow sensitive detection. However, if N_2O diluted with N_2 or Ar is used, the lifetime of e_{aq}^- becomes ~100 ns and the absorption can readily be detected. When the absorption is monitored at 590 nm where there is no signal due to I_2^-, the e_{aq}^- formed with the first laser pulse is easily detected. However, no electrons that might have been formed by photodetachment from I_2^- by 355-nm light at the second laser pulse were seen. Our detection sensitivity at 590 nm corresponded to an optical density of ~0.002 and the yield of I_2^- photolyzed to an optical density of ~0.06 at 380 nm. Since the extinction coefficient of e_{aq}^- at 590 nm and that of I_2^- at 380 nm are similar, even a ~3% yield of photoelectrons could have been detected. Combined with the quantum yield of I_2^- dissociation, this value gives an upper limit of 0.004 for the absolute quantum yield of photodetachment.

TABLE I: Quantum Yields for Dissociation and Recovery Rate Constants

species	quantum yield[a,b]	rate constant,[c] M^{-1} s^{-1}
Cl_2^-	0.25	8×10^9
Br_2^-	0.15	9×10^9
I_2^-	0.12	1.1×10^{10}
$(SCN)_2^-$	0.07	9×10^9

[a] Determined as described in the Experimental Section for 355 nm except for $(SCN)_2^-$ at 532 nm. The reference system for 355 nm was benzophenone triplet, ϵ_{530} = 7500 M^{-1} cm^{-1} (Bensasson, R. V.; Land, E. J. In "Photochemical and Photobiological Reviews"; Smith, K. C., Ed.; Plenum Press: New York, 1978; Vol. 3, p 163) and $\phi = 1$ (Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129). The reference for 532 nm was tris(2,2′-bipyridyl)ruthenium(II) chloride triplet, ϵ = 17 000 M^{-1} cm^{-1} and $\phi = 1$ (Kumar, C. V.; Davis, H. F.; Das, P. K. *Chem. Phys. Lett.* **1984**, *109*, 184). [b] Estimated error ±20%. [c] Estimated error ±10%.

TABLE II: Extinction Coefficients Used in Calculations[a]

species	λ, nm	ϵ, M^{-1} cm^{-1}
Cl	337	4000
	340	3800
	355	2700
	360	2400
Cl_2^-	337	9000
	340	9000
	355	7100
	360	6200
Br_2^-	355	9500
	380	8700
I_2^-	355	8500
	380	9400
SCN_2^-	500	6800
	532	4500

[a] Based on the spectra from the papers in ref 1, except for Cl which was determined as described in the text.

Br_2^- was photolyzed at 355 nm and absorption monitored at 380 nm. The results obtained were very similar to those for I_2^-. A bleach and a subsequent complete exponential recovery were seen. The rate constant for recombination was determined from a plot of pseudo-first-order rate vs. concentrations to be 9×10^9 M^{-1} s^{-1} in agreement with past determinations.[9] No photoelectrons were observed even when the concentration of $Na_2S_2O_8$ was kept at 1 mM in order to decrease the rate of reaction of the electrons with it. The lifetime expected for electrons under this condition is ~100 ns. The red absorption band of Br_2^- was not excited because the optical density at these wavelengths is very small.

$(SCN)_2^-$. The absorption of $(SCN)_2^-$ is in the visible[4] so that it could be photolyzed at 532 nm (ϵ ~ 4500 M^{-1} cm^{-1}) and the absorption monitored at 500 nm (ϵ ~ 6800 M^{-1} cm^{-1}). Excitation of $(SCN)_2^-$ results in a bleach and a subsequent exponential

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(10) Treinin, A.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 1716.

recovery back to the original absorption level. The quantum yield is similar to that for the halide systems. A plot of recovery rate vs. [SCN^-] is a straight line with a second-order rate constant of 9×10^9 M^{-1} s^{-1}; the recovery should, as in the other cases, correspond to the recombination process. This clearly suggests that photodissociation of $(SCN)_2^-$ prevails. This rate constant is not independently known and represents a valuable addition to the mechanism of formation of $(SCN)_2^-$ from OH and SCN^-. The value used by Behar et al.[4] is 6.8×10^9 M^{-1} s^{-1}. Because the absorption of SCN is in a convenient region where that of $(SCN)_2^-$ is very small (330 nm),[4] the photodissociation can also be monitored by the formation of SCN. Thus, $(SCN)_2^-$ is different from the halides case where the absorption of the atom either falls in regions where our analyzing lamp intensity is very small (λ_{max} for I is 260 nm and for Br 275 nm) or overlaps the X_2^- absorption as is the case of the Cl atom (to be discissued in detail; see below). At the time of the first laser, the absorption at 330 nm showed a rapid rise and then rounding and an exponential decay of absorption whose rate increases linearly with [SCN^-]. This behavior is explainable by the sequence of reactions forming SO_4^-, SCN, and finally $(SCN)_2^-$. At the time of the second laser pulse there was a step *increase* in absorption which decayed exponentially at a rate depending linearly on [SCN^-]. The increase in absorption must correspond to the production of SCN in the photolysis of $(SCN)_2^-$. The decay of SCN should have the same rate constant as that for recovery of $(SCN)_2^-$ absorption since they both correspond to the same process, reaction 3. This expectation was confirmed by plotting pseudo-first-order rate constants for both processes against SCN^- concentration in a single plot. No difference between the two sets of data was discernible. Thus, photodissociation of $(SCN)_2^-$ is confirmed kinetically as well as spectroscopically.

These results also strengthen the assignment of the spectrum of SCN radical.[4] The increase in absorbance at 330 nm (0.0066) was found to be 0.18 of the bleach (0.037) at 500 nm. Using a value of ϵ_{500} for $(SCN)_2^-$ of 6800 M^{-1} cm^{-1} leads to $\epsilon_{330} = 1200$ M^{-1} cm^{-1} for SCN radical if $(SCN)_2^-$ does not absorb appreciably at 330 nm. (The curves in ref 4 show little absorption here.) The value given in ref 4 is 900 M^{-1} cm^{-1} which is dependent on the rate constants for the various reactions. In the case of $(SCN)_2^-$ as for the halide systems, no evidence for photoionization was found. Hence, photodissociation is considered the only pathway. Since the structure of $(SCN)_2^-$ in solution has been established to be $(N{\equiv}C{-}S{-}S{-}C{\equiv}N)^-$,[11] the results require that the potential energy surface along the S–S nuclear coordinate in the first allowed excited state of $(SCN)_2^-$ be repulsive.

Cl_2^-. For most of this study the radical was photolyzed at 355 nm and observation was at 340 nm. When the nitrogen laser was used, observation was at 360 nm. As in the other cases, a search was made for photoelectrons at lower concentrations of $S_2O_8^{2-}$ but none was detected. The quantum yield of the initial bleach was found to be 0.2 after correction for the absorption by the Cl atom produced and the latter's partial photolysis (see below). This system is different from those above in that even though one sees an initial bleach with the absorption recovering exponentially, the recovery is not complete. In fact, at the same laser power and fluence level used (this was made sure by not modifying the optics in any way while the iodide or bromide solution was replaced with chloride solution) the recovery of absorption is only half complete (Figure 4, curve a). After the initial growth the absorption level stays flat for a few microseconds. At longer times, however, the signal is distorted. The base line subtraction procedure assumes that the second-order disappearance processes are the same with and without the second laser. To a first approximation this will be true, but because some Cl_2^- has been converted into other species, a difference can be expected. Hence, a slow growth of absorption is artifically introduced into the recovery curves. A plot of the rate of initial recovery vs. [Cl^-] is a straight line passing through the origin. The slope must, as in the other cases, correspond to the recombination reaction (3), and the rate constant so determined is 8×10^9 M^{-1} s^{-1}. The zero intercept shows that the loss of absorption cannot be due to any chemical process such as $Cl + H_2O \rightarrow OH + Cl^- + H^+$ that competes directly with the reaction of Cl atoms and Cl^- because the pseudo-first-order rate constant of the competing process would appear as the intercept of this plot. However, not all the Cl atoms produced react with Cl^-, implying that a fraction of the atoms produced are intercepted at some stage. The net loss of absorption must be due to formation of a product long-lived on the microsecond time scale that absorbs less than Cl_2^- or does not absorb at all. A photobleaching spectrum obtained by plotting the optical density at the flat region as a function of monitoring wavelength was identical with the absorption spectrum of Cl_2^- over the region scanned (300–700 nm) and revealed no extra features. (Above about 450 nm no absorption or bleach was seen at the time of the second laser.) The only probable species that can be formed from Cl atoms which has an absorption spectrum very similar to that of Cl_2^- is $ClOH^-$.[1c] However, any $ClOH^-$ formed would immediately dissociate to give Cl^- and OH in less than 1 ns at the pH of our solutions (pH ~3.5).[1c] The only other probable product (which must be a radical) is OH, which does not absorb above 300 nm. Under more acidic conditions, OH is converted to Cl_2^- so that addition of acid should bring about more recovery of the absorption signal. Figure 4 shows the effect of adding acid. Since reaction of charged species will be sensitive to the total ionic strength of the solution, the ionic strength was maintained at a constant value by adding calculated quantities of $NaClO_4$. The recovery curves now show fast and slow components. These gradually merge as the pH decreases. The initial fast growth is, of course, the recombination of Cl atoms with Cl^-. The second part, whose rate increases with addition of more acid, is the conversion of OH to Cl_2^- by the known mechanism[1c] involving H^+. The rate semiquantitatively matches that expected, but no detailed analysis was made. The effect of acid chemically confirms that the loss of absorption arises as a result of OH radicals replacing Cl_2^-. These OH radicals could not have been formed from Cl atoms reacting with water in competition to their reaction with Cl^- because the reported rate is too slow[1c] and competition with recombination has been ruled out above.

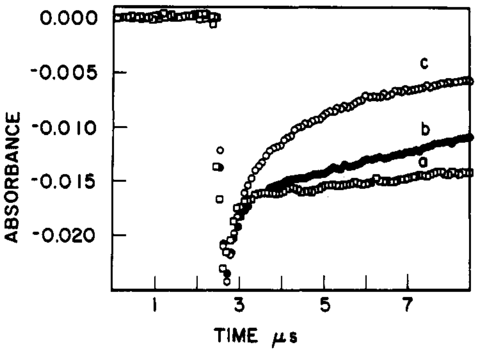

Figure 4. pH dependence of the bleach signal at 340 nm for 0.5 mM NaCl solution (total ionic strength 0.15 M): (a) pH 3.75, (b) pH 1.77, and (c) pH 1.20 (average of 25 shots each).

The variation in bleaching behavior with laser intensity gives a clue to the reactions involved. The initial bleach was found to vary linearly with laser intensity whereas the ratio of "net loss of absorption" to bleach, normalized to constant [Cl_2^-], was found to be a nonlinear function of the laser intensity (Figure 5). If the process responsible for the loss signal were monophotonic, then the log–log plot in Figure 5 would be a straight line parallel to the intensity axis. Given the moderate laser energies, such a nonlinear behavior can only be consistent with a sequential excitation involving a real intermediate. For the same reason involvement of more than two photons is considered highly unlikely even though it is not apparent from the figure just how many photons per molecule are involved in OH production. In summary, photodissociation of Cl_2^- is monophotonic and a product of the first photolysis apparently is photolyzed to give OH. At this point, it is appopriate to consider the exact sequence of reactions by

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[11] Wilbrandt, R.; Jensen, N. H.; Pagsberg, P.; Sillesen, A. H.; Hansen, K. B.; Hester, R. E. *Chem. Phys. Lett.* **1979**, *60*, 315.

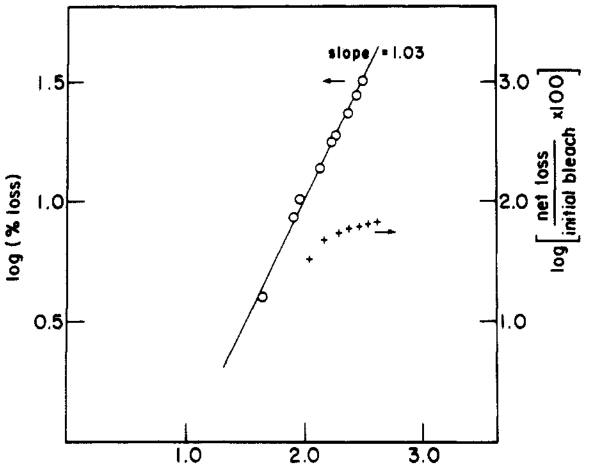

Figure 5. Intensity dependence of bleach and loss signals (see text). The bleach is defined as the initial amplitude immediately following the laser pulse, and the loss is the amplitude after the fast exponential recovery. (In Figure 4a the bleach is about 0.023 in absorbance and the loss is about 0.016.)

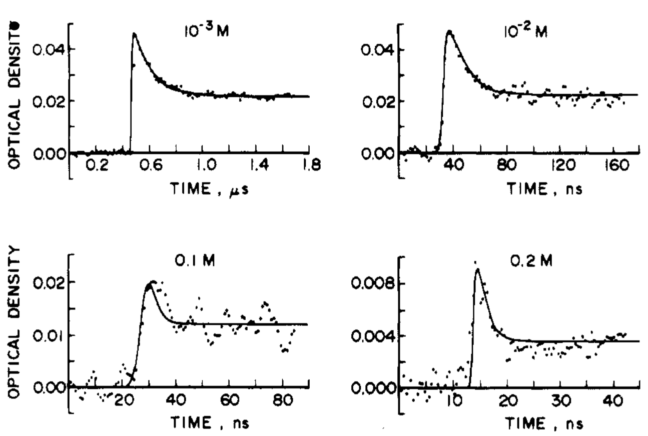

Figure 6. Experimental bleach signals (inverted) observed at 340 nm for 0.001 M (25 shots), 0.01 M (15 shots), and 0.1 M (50 shots) and at 360 nm for 0.2 M (50 shots) NaCl solutions. The first three sets are for 355-nm excitation, and that for 0.2 M is for 337-nm excitation with a 0.8-ns pulse. The calculated curves were obtained by numerically integrating the differential equations corresponding to the sequential reactions (8)–(10). The values of the parameters are given in the text.

reference to the potential energy diagram in Figure 1. The sequence of steps in the initial photolysis is

$$Cl_2^-(^2\Sigma_u^+) \xrightarrow{h\nu} \{Cl_2^-(^2\Sigma_g^+)\} \rightarrow Cl^-(^1S_0) + Cl(^2P_{1/2}) \quad (4)$$

$$Cl(^2P_{1/2}) \rightsquigarrow Cl(^2P_{3/2}) \quad (5)$$

$$Cl(^2P_{3/2}) + Cl^- \rightarrow Cl_2^-(^2\Sigma_u^+) \quad (6)$$

It should be noted that because the initial Cl atom ($^2P_{1/2}$) correlates only with the dissociative $^2\Sigma_g^+$ state of Cl_2^-, it cannot react with Cl^-. The spin–orbit splitting in Cl is 882 cm^{-1},[12] and in the gas phase, quenching of the $^2P_{1/2}$ level by H_2O has been found to have a rate constant of $\sim 2.5 \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} at 300 K.[13] Assuming the same mechanism of quenching in the liquid phase, we obtain a lifetime of ~10 ps for $Cl(^2P_{1/2})$ in liquid water. The low dissociation quantum yield on the nanosecond time scale (0.2) suggests either that relaxation of the atom competes with separation of Cl and Cl^- or that some other fast relaxation occurs to the ground molecular state.

Simultaneous two-photon excitation of $Cl_2^-(^2\Sigma_u^+)$ was considered but rejected on the ground that there is no known two-photon-resonant, allowed state for this photon energy. Much more likely is photolysis of the chlorine atom. The ground-state Cl atom has a charge transfer from solvent (CTFS) band in the UV with $\lambda_{max} = 320$ nm.[10] This spectrum was redetermined by photolysis of a solution of Cl_2 in water at 355 nm. Approximately 2.3 M perchloric acid containing ~0.001% Cl^- was added ($[Cl^-] \sim 80$ μM) to prevent hydrolysis of Cl_2. An initial step rise followed by a slow growth due to the Cl^- still present in the solution was observed. The absorption spectrum was taken at the initial rise. The extinction coefficient of Cl atom was determined by adding a calculated amount of Cl^- and using the known value of $\epsilon_{340} = 9000$ M^{-1} cm^{-1} for Cl_2^- as a reference; ϵ_{340} for Cl atom was found to be 3800 M^{-1} cm^{-1}. Our spectrum and ϵ_{340} value agree with those of Hayon and Treinin.[10] The charge-transfer state has been predicted to have a structure such as[9] $Cl \cdots O{-}H_2$, and it would thus lead to the sequence of reactions

$$Cl \cdots O{-}H_2 \xrightarrow{h\nu} Cl^- + H_2O^+ \rightarrow Cl^- + H^+ + OH \quad (7)$$

It should be possible to kinetically compete with excitation of Cl by the second photon by using high concentrations of Cl^- if it is the ground state of the chlorine atom which is being photolyzed. When the lifetime of Cl is made shorter than the laser pulse width, its concentration will decrease and the permanent loss of absorption will drop dramatically. In addition, Cl_2^- will be rapidly re-formed, reaching a steady-state concentration, and the amount of bleach will also decrease.

Certain precautions were taken to reduce the uncertainties involved in the high $[Cl^-]$ experiment in order to make the analysis more meaningful. First, the data had to be corrected for true I_0 values (see the Experimental Section). Second, at high $[Cl^-]$ and the natural pH (~3.5) of the 5 mM persulfate solution, conversion of OH to Cl_2^- will occur and a slow recovery such as seen in Figure 4 in highly acidic but low $[Cl^-]$ solutions will complicate the analysis. For this reason it is best to operate at near-neutral pH's. The pH was adjusted by adding KOH to the solution. Data obtained under these conditions are shown in Figure 6 as solid circles. Note the differing time scales and the fact that the data for 0.2 M Cl^- were taken with the 0.8-ns laser which provides a lower dose. Experiments were performed with 355-nm excitation up to 200 mM Cl^- and for 10, 100, and 200 mM Cl^- with the short-pulse nitrogen laser. It is seen that the bleach and loss amplitudes decrease as $[Cl^-]$ increases, but at the same time, even for $[Cl_2^-] = 200$ mM, where the half-life of Cl atoms is only 0.6 ns, the loss of absorption is considerable. In order to understand this behavior, differential equations corresponding to the various steps involved were set up. These coupled equations were integrated numerically. The sequence

$$Cl_2^- \xrightarrow{h\nu} Cl + Cl^- \quad (8)$$

$$Cl \xrightarrow{h\nu} \text{product} \quad (9)$$

$$Cl + Cl^- \rightarrow Cl_2^- \quad (10)$$

was used. Most parameters needed for the numerical solution such as the recombination rate constant and extinction coefficients at 355 and 340 nm of Cl_2^- and Cl are known (see Table II). The quantum yield for dissociation of Cl_2^- was determined as described in the Experimental Section; the value found, 0.25 at 355 nm, was used in the calculation. The laser pulse shape for 355-nm excitation was modeled as a Gaussian curve with width (fwhm) of 5 ns and that for 337-nm excitation a width of *0.8* ns. In the latter experiments, a time constant of *1.5* ns for the photomultiplier and digitizer combined was obtained from the response to scattered laser light.

The adjustable parameters are the product of dose and quantum yield for Cl_2^- dissociation and the ratio of quantum yield for Cl photolysis to that for Cl_2^-. The parameter corresponding to dose was adjusted to give the correct initial bleach for the lowest millimolar Cl^- concentration. All other dose values were calculated from this value and the measured relative dose. The quantum yield for Cl atom photolysis (reaction 9) was adjusted to give the correct loss of absorption. This value was kept constant for all

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other Cl^- concentrations. The value was found to be 0.185 times that for Cl_2^- or 0.46. The calculated curves in Figure 6 are seen to match the experimental points. Data for lower concentrations of Cl^- were taken with the nitrogen laser and treated in the same way, but only that for the highest Cl^- concentration (200 mM) is shown. Because the calculated curve fits well here, *including the time dependence*, it is clear that no precursor ($^2P_{1/2}$ Cl atom) with a lifetime comparable to the pulse width (1 ns) can be involved.

The absence of any delay in recombination on the 1-ns time scale is in agreement with the small quantum yield of dissociation which implies that the $^2P_{1/2}$ atom (which cannot react with Cl^- to give Cl_2^-) does not have any significant lifetime even at the time scale of the diffusive separation of Cl and Cl^-. The other halides share the same state correlation diagram and have similar quantum yields so that relaxation of the $^2P_{1/2}$ atom appears to be fast in all cases. In the case of I atom the gas-phase quenching of the $^2P_{1/2}$ atom by H_2O[14] is slightly slower than in the case of Cl (calculated lifetime in liquid water 30 ps for I vs. 10 ps for Cl) which is not reflected in the quantum yield. Alternatively, as suggested above, relaxation of the excited state occurs before full separation into the two fragments.

In no case was photodetachment observed even though a small yield was reported for Cl_2^- in the gas phase.[2c] On the one hand, solvation of the X_2^- will lower the energy of X_2^- and increase the energy necessary to detach the electron. Counter to this effect is the reduction in energy provided by the solvation of the e_{aq}^- formed. (The photoionization of neutral species in water occurs at much lower energies than under vacuum.) In the case of Cl_2^-, where the vertical ionization potential is 4.0 eV,[2d] the energy of the photon (3.49 eV) may not be enough to cause photodetachment in the liquid phase. The lowered electron affinity for Br_2 and I_2 would make detachment more likely in those cases although, in fact, none was seen.

Summary

Photolysis of several radicals of the type X_2^- in aqueous solution has been experimentally demonstrated. The results have proved to be of value in understanding the nature of the absorption bands. Dissociation has been found to be the main process with a quantum yield of ~0.1–0.2 with no photodetachment detected in any case. Both absorption bands of I_2^- behave similarly and lead to dissociation. For each system it was possible to measure the rate constant for the recombination providing direct measurements in cases where such data had previously been obtained only indirectly.

In the case of Cl_2^-, the Cl atom produced also absorbs a photon yielding OH as shown by the effect of added acid on the absorption recovery kinetics. Observation of this reaction confirms the nature of the absorption observed for Cl as charge transfer from solvent. A direct implication of this result is that photolysis of the other atoms which were discussed by Treinin and Hayon[10] (Br, I, and H) would also lead to production of OH by oxidation of water. Oxidation of water by photolysis of H atom which is a reducing species is an interesting suggestion even though it would be difficult to establish because of the weak absorption and short wavelength (~200 nm). It is suggested that picosecond photolysis of X_2^- would bring a number of new aspects to the discussion of recombination reactions because an excited electronic state of the halide atom is produced. In the widely studied example of $I + I \rightarrow I_2$, the atoms are not produced in their excited states, and so electronic relaxation of atoms need not be considered.

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RC-PID: A Control Algorithm Suitable for Precise Rate Determinations[†]

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The RC-PID or rate-compensated proportional–integral–derivative control algorithm is an improvement to the usual PID algorithm. The RC-PID algorithm is analyzed by consideration of the system response function, and comparison is made to two common control functions. The applicability of the RC-PID algorithm to high-precision rate studies is considered, and comparison is made to an earlier implementation.

Introduction

Direct titration of a chemical reaction in order to maintain an experimental observable constant yields, in principle, the reaction rate. A common application of this approach is the pH stat, where hydrogen ion or hydroxide ion produced by a chemical reaction is titrated by a standardized base or acid solution in a manner so as to keep the pH constant. This technique requires some form of feedback control in order to determine the appropriate rate of titrant addition. Such "X"-stat techniques are potentially powerful methods for determination of reaction rates, especially for those systems which do not have another convenient observable. Nevertheless, these techniques have not recently been popular. One reason for their underutilization has been the inaccuracies attendant to the method of feedback control. Of the two common control functions, neither on/off nor simple proportional yields satisfactory rate estimates under all circumstances, as was recognized by Jacobsen et al.[1] This problem leads to a significant operator dependence of the determined rates and thus the relegation of the device to lower accuracy applications. The development of suitable control functions has been hampered by the common use of only one titrant, with the notable exception of coulometric generation of both hydroxide ion and hydrogen ion in the same reaction vessel.[2] Additionally, analog controllers lack the ability to "remember" the history of a given titration, which limits the potential sources of information available for control.

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