The Reaction of e_{vis}^- and e_{ir}^- with Cl_2^- in LiCl/D$_2$O Glasses as Measured from 10^{-7} to 2100 s

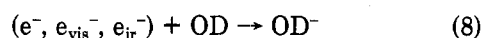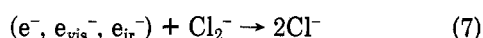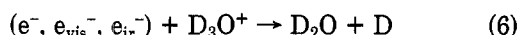**Norman V. Klassen,* Richard J. Adams, George G. Teather, and Carl K. Ross**

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In order to assess the importance of the reaction of trapped electrons (e_{vis}^- and e_{ir}^-) with Cl_2^- in LiCl/D$_2$O glasses at 72 K, we monitored the concentration of each species continuously from 10^{-7} to 2100 s following single radiation pulses. The decay of e_{vis}^-, both in the absence of light and during photobleaching, seems to occur almost entirely by reaction with Cl_2^-. However, reaction of e_{ir}^- with Cl_2^- does not seem to take place. Conversion of e_{ir}^- into e_{vis}^-, with an efficiency of $\geq 6\%$, has been observed in LiCl glasses for the first time.

Introduction

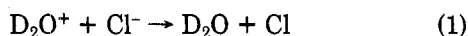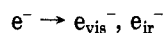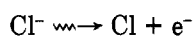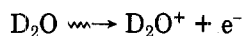The radiolysis of aqueous LiCl glasses has been widely studied.[1-7] The only species observed by optical absorption are the trapped electrons, e_{vis}^- ($\lambda_{max} \sim 600$ nm) and e_{ir}^- ($\lambda_{max} > 3200$ nm), and Cl_2^- ($\lambda_{max} \sim 340$ nm). The following reactions, along with others, probably take place in irradiated LiCl/D$_2$O glasses:

$$D_2O \rightsquigarrow D_2O^+ + e^-$$

$$Cl^- \rightsquigarrow Cl + e^-$$

$$e^- \rightarrow e_{vis}^-, e_{ir}^-$$

$$D_2O^+ + Cl^- \rightarrow D_2O + Cl \tag{1}$$

$$D_2O^+ + D_2O \rightarrow D_3O^+ + OD \tag{2}$$

$$OD + Cl^- \rightarrow OD^- + Cl \tag{3}$$

$$Cl + Cl^- \rightarrow Cl_2^- \tag{4}$$

$$(e^-, e_{vis}^-, e_{ir}^-) + D_2O^+ \rightarrow D_2O \tag{5}$$

$$(e^-, e_{vis}^-, e_{ir}^-) + D_3O^+ \rightarrow D_2O + D \tag{6}$$

$$(e^-, e_{vis}^-, e_{ir}^-) + Cl_2^- \rightarrow 2Cl^- \tag{7}$$

$$(e^-, e_{vis}^-, e_{ir}^-) + OD \rightarrow OD^- \tag{8}$$
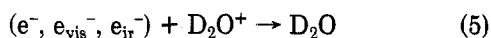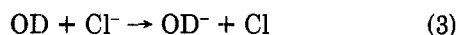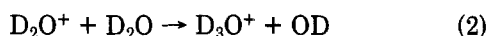
The decay of both e_{vis}^- and e_{ir}^- has been observed following the pulse radiolysis of scavenger-free LiCl glasses[1-3] but the reactions causing this decay have not been ascertained. This report assesses the importance of the reaction with Cl_2^- (reaction 7) at 72 K in 12, 9.5, and 6 M LiCl/D$_2$O. Over this range of LiCl concentrations both the radiation yields of e_{vis}^- and e_{ir}^- and their decay rates vary considerably. Because of the vastly different time scales over which substantial decay of e_{vis}^- and e_{ir}^- occur it was decided to monitor e_{vis}^-, e_{ir}^-, and Cl_2^- continuously from 10^{-7} to 2100 s. This was accomplished with a computer-controlled light detection system.

Experimental Section

Solutions were prepared from anhydrous LiCl (Baker, Analyzed Reagent) and D$_2$O (Merck Sharp and Dohme, 99.7 atom % D) and bubbled for 20 min with argon (Liquid Air Ltd., SUPR grade) before being sealed off in quartz (Suprasil) cells with a 5-mm optical path length. Glasses were formed by slowly lowering the cells into liquid nitrogen. The samples were irradiated at 72 K in a dewar with Suprasil optical windows. A regulated flow of helium through the liquid nitrogen maintained the temperature at 72 K and avoided bubbles in the light path. Only freshly dissolved solutions of LiCl were used since there was some

indication that trapped electrons decay more rapidly in glasses made from old solutions.

Free-standing windowless samples of 9.5 M LiCl glasses with a 5-mm light path were also made. These samples were made in holders with stainless steel sides which were easily removed after bubbling the solution and making the glass. The stainless steel plates were lightly coated with paraffin wax to produce a nonwettable surface. The surfaces of the glasses, after knocking off the plates, were highly charged and strongly attracted any ice particles in the liquid nitrogen. The charge was eliminated by removing the samples from liquid nitrogen for several seconds and scraping the surfaces with the edge of a microscope slide, a procedure which probably melted a thin layer on the surface.

Some of the experimental equipment and procedures have been described previously.[1-3,8,9] The spectra at 100 ns were measured at individual wavelengths following single 40-ns pulses of 36-MeV electrons from a linear accelerator. The analyzing light source was a pulsed 900-W xenon arc. Three light detectors were used, a Philips XP1003 photomultiplier for wavelengths from 300 to 650 nm, an EG&G SHS-100 silicon photodiode from 450 to 1000 nm, and a Barnes A-100 indium arsenide photodiode from 900 to 2300 nm. The detector signal was measured with a Tektronix R7912 transient digitizer and computer-stored for futher use. The decays at 1800, 650, 550, and 350 nm between 10^{-7} and 10^{-3} s were measured in the same way as the 100-ns spectrum except that the analyzing light passed through an interference filter of the appropriate wavelength before reaching the sample. This was found to eliminate photobleaching by the analyzing light. The slower the sweep the more important it was to subtract from the signal the shape of the light pulse in the absence of a radiation pulse. This was easily done with the transient digitizer computer system.[8]

Miller et al.,[10] Nosaka et al.[11] and Kumar and Neta[12] have described methods of measuring transient absorptions over many decades of time. Our method of measuring between 10^{-3} and 2100 s is substantially different from their methods, necessitated in part by our desire to measure the transients for 0.5 h in order to relate the results directly to measurements made on a Cary spectrophotometer. In order to extend the time scale to this extent we found it necessary to correct for variations in analyzing lamp intensity. The analyzing light source was a regulated tungsten–iodine lamp in a light-tight housing with an aperature consisting of an electronic shutter. An interference filter limited the light incident on the sample to the wavelength being studied. The analyzing light intensity was monitored by sampling the light before the sample

with a light guide which led to a United Detector Technology PIN 10/UV Si photodiode through a suitable interference filter. This reference signal, with a 550-, a 650-, or a 900-nm filter in place, was used to correct for variations in the lamp output at 350 or 550 nm, at 650 nm, and at 1800 nm, respectively. The correction was calibrated in the absence of a radiation pulse. A previously unirradiated sample at 72 K was given a single 2-μs pulse of ~25 krd. The computer opened the electronic shutter just before the radiation pulse and recorded the analyzing light and reference light signals. The electronic shutter remained opened for 1 s following the pulse and both light levels were recorded about four times for each decade of time beginning at 1 ms after the pulse. After the first second the shutter was only opened for periods of 15 ms at predetermined times. In this mode the detector signals were recorded just before and during "light-on" to permit corrections for the dark current of the detectors.

Dosimetry was carried out with oxygen-saturated 5 × 10^{-3} M KSCN solutions in the same cells used to hold the samples and irradiated in the same dewar with methanol surrounding the cell rather than liquid nitrogen. A value of 2.2 × 10^4 was used for $G\epsilon_{475}(SCN)_2^-$. Corrections were applied for the electron densities of the samples used. Dosimetry for the windowless samples were carried out in the windowless holder by attaching two Suprasil plates to the holder in order to contain the dosimeter solution.

Spectra were also measured at 2100 s with a Cary 17 spectrophotometer which selects the analyzing light wavelength ahead of the sample, thus avoiding photobleaching. A blank was measured with the unirradiated sample. The sample was then irradiated in the dark with one or more 40-ns pulses (10–48 krd) and transferred back to the Cary. An attampt was made to maintain the temperature at 72 K even during the transfer. The difference between the blank and the spectrum after irradiation should represent the absorption spectrum produced by irradiation. Often, however, the background spectrum after irradiation was slightly different than the initial blank, due perhaps to misalignment. Therefore, the blank was corrected by a constant absorbance change across the whole spectrum, the extent of the correction being determined by assuming that $G\epsilon_{900}(e_{vis}^-)/G\epsilon_{max}(e_{vis}^-) = 0.1$ and proceeding iteratively to a new value of the blank at 900 nm. This method led to reproducible results and was preferred over the method of determining a blank by exhaustively photobleaching the sample, since the last traces of Cl_2^- were very difficult to bleach. After measuring the absorption spectrum, the samples were bleached for 5 min with a tungsten–iodine lamp, with or without a 450-nm cut-on filter, in such a manner that the intensity of the bleaching light was approximately the same each time. The spectrum was remeasured after a temperature of 72 K had been reestablished.

Results

12 M LiCl/D$_2$O. The spectrum of irradiated 12 M LiCl/D$_2$O was measured 100 ns after the start of a 40-ns pulse. It was also measured after 2100 s with a Cary spectrophotometer. These spectra are shown in Figure 1. The 2100-s spectrum was normalized to the value of $G\epsilon_{650}$ found by following the decay at 650 nm from 100 ns to 2100 s (Figure 2). The band with $\lambda_{max} > 2500$ nm is due to e_{ir}^-. The value of $\lambda_{max}(e_{vis}^-)$ is 625 nm at 100 ns and 570 nm at 2100 s. The λ_{max} of the band due to Cl_2^- is ~340 nm. The values of $G\epsilon$ for the 100-ns spectrum were measured directly by thiocyanate dosimetry.

The decay curves at 1800, 650, 550, and 350 nm are shown in Figure 2. The data points between 10^{-7} and 10^{-3}
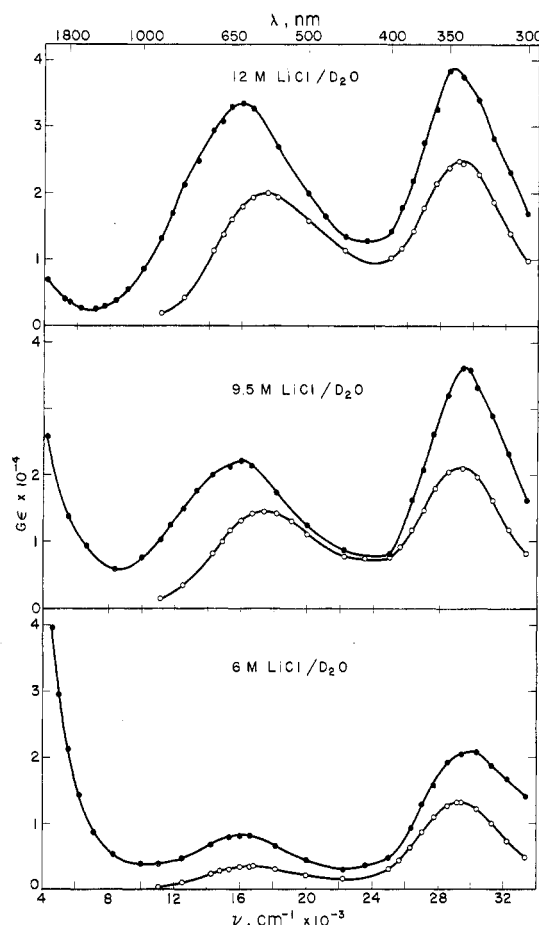

Figure 1. Absorption spectra for Irradiated LiCl/D$_2$O glasses at 72 K. The ● were measured at 100 ns after the start of a 40-ns pulse. The O were measured at 2100 s after one to six 40-ns pulses. All samples were contained In Suprasil cells.

TABLE I: Yields^a of Cl$_2^-$, e$_{vis}^-$, and e$_{ir}^-$ at 100 ns, 72 K

glass	$G(Cl_2^-)$	$G(e_{vis}^-)$	$G(e_{ir}^-)$
12 M LiCl/D$_2$O	3.80	1.67	0.28
9.5 M LiCl/D$_2$O	3.59	1.11	1.06
6 M LiCl/D$_2$O	2.16	0.42	1.63

^{a} Details of the calculations are given in the text.

s are representative points taken from oscilloscope traces. The points after 10^{-3} s represent individual measurements. It is obvious that the 350-nm curve suffers from serious scatter. In part, this is due to our inability to completely correct for differences in the efficiency of the photomultiplier between conditions of initial light-on (~1 s) and intermittant light (15 ms). Envisaged experimental changes to reduce the initial light-on to 0.05 s should largely eliminate this source of scatter.

In view of the scatter in the 350-nm decay measurements (Δ) at long times, we consider the solid triangle (▲) at 2100 s, taken from Figure 1, to more accurately represent the value of $G\epsilon_{350}$ at 2100 s. Several sources of error could have contributed to the 6% difference between the Δ and ▲ at 2100 s. The problem of data scatter has been discussed. In addition, a comparison of Δ and ▲ involves data taken from three separate samples with the inherent differences this can cause. Lastly, the temperature control is believed to have been better than 72 ± 2 K but temperature differences could have had some effect since there were indications that, in the range 72–77 K, the decay at 350 nm has a higher activation energy than the decay at 650 nm.

The values of $G(Cl_2^-)$, $G(e_{vis}^-)$, and $G(e_{ir}^-)$ at 100 ns are given in Table I. They were calculated from the data in
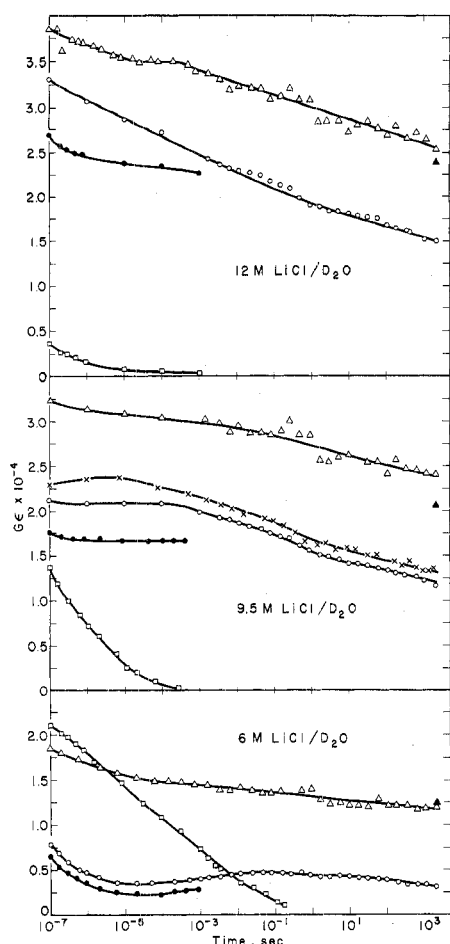
Figure 2. Optical absorption changes at selected wavelengths in irradiated LiCl/D_2O glasses at 72 K. The □ correspond to 1800 nm, O to 650 nm, ● to 550 nm, △ to 350 nm for samples in Suprasil cells. The ▲ corresponds to $G\epsilon_{350}$ at 2100 s as shown in Figure 1. The × correspond to 650 nm with windowless samples.

TABLE II: Decay of e_{ir}^-, e_{vis}^-, and Cl_2^- at 72 K

quantity decayed	decay[a] in time interval of	
	10^{-7}–10^{-4} s	10^{-4}–2100 s
12 M LiCl/D_2O		
$\Delta G(Cl_2^-)$	0.32	1.13
$\Delta G(e_{vis}^-)$	0.25	0.43
$\Delta G(e_{ir}^-)$	0.26	0.02
9.5 M LiCl/D_2O		
$\Delta G(Cl_2^-)$	0.14	1.28
$\Delta G(e_{vis}^-)$	0.02	0.36
$\Delta G(e_{ir}^-)$	1.02	0.04
6 M LiCl/D_2O		
$\Delta G(Cl_2^-)$	0.39	0.28
$\Delta G(e_{vis}^-)$	0.23	0.01
$\Delta G(e_{ir}^-)$	0.78	0.85

[a] Decays measured in units of ΔG, i.e., decrease in G over time interval indicated.

TABLE III: Photobleaching[a] of e_{vis}^- and Cl_2^- at 72 K

bleaching light	% e_{vis}^- bleached	$\Delta G(Cl_2^-)/\Delta G(e_{vis}^-)$[b]
12 M LiCl/D_2O		
full light	75	1.2
>450 nm	85	1.0
9.5 M LiCl/D_2O		
full light	93	1.3
>450 nm	93	1.2
6 M LiCl/D_2O		
full light	87	1.2
>450 nm	73	1.0

[a] Each bleaching was carried out for 5 min with a tungsten–halogen lamp under conditions such that the light flux was approximately the same each time. The bleaching was done with or without a 450-nm cut-on filter as indicated. [b] ΔG represents the bleaching yield. $\Delta G(Cl_2^-)$ was measured at λ_{max} = 343 nm after correcting for the absorption due to e_{vis}^- by assuming that $\epsilon_{343}(e_{vis}^-)/\epsilon_{max}(e_{vis}^-)$ = 0.15. $\epsilon_{max}(Cl_2^-)$ was taken to be 0.88×10^4 M^{-1} cm^{-1}.

Figure 1 by assuming that $\epsilon_{1800}(e_{ir}^-)$ = 1.3×10^4 M^{-1} cm^{-1},[3] that $\epsilon_{max}(e_{vis}^-)$ = 2×10^4 M^{-1} cm^{-1},[1] that $\epsilon_{max}(Cl_2^-)$ = 0.88 $\times 10^4$ M^{-1} cm^{-1},[13] and that $\epsilon_{340}(e_{vis}^-)/\epsilon_{max}(e_{vis}^-)$ = 0.15. The latter ratio corresponds to the value in 10.7 M BeF_2/D_2O glass at both short and long times.[14] We chose 10.7 M BeF_2/D_2O because the spectral shift of $\lambda_{max}(e_{vis}^-)$ from 630 nm at 100 ns to 560 nm at long times[14] is almost identical with the shift observed in LiCl glasses and because there seems to be no interfering absorption at 340 nm in BeF_2 glasses. The small contribution expected from Cl_2^- at 650 nm[15] has been neglected. The values in Table I are higher than previously published values at 100 ns.[2] On the other hand, the values of $G\epsilon_{694}$ for 9.5 and 12 M LiCl at 2100 s (Figure 1) are lower than the corresponding values measured at 10–30 min by Nguyen and Walker.[6] It seems that experimental procedures such as the rate of cooling and the freshness of solutions may significantly affect the values of $G\epsilon$. The glasses used in this study were prepared by a standard procedure and each result in Table I came from several samples and seemed to be reproducible.

In a similar manner, the values of $G(Cl_2^-)$, $G(e_{vis}^-)$, and $G(e_{ir}^-)$ were calculated for 10^{-4} and 2100 s from Figures 1 and 2. The value of $G(Cl_2^-)$ at 10^{-4} s was calculated from the solid line in Figure 2 whereas its value at 2100 s corresponds to the solid triangle for reasons given above. Since $\lambda_{max}(e_{vis}^-)$ was not determined directly at 10^{-4} s the small shift from 625 nm was estimated from the changes in the ratio of $G\epsilon_{550}/G\epsilon_{650}$ (see Figure 2). The changes in $G(Cl_2^-)$, $G(e_{vis}^-)$, and $G(e_{ir}^-)$ during the time intervals 10^{-7}–10^{-4} and 10^{-4}–2100 s are given in Table II.

After measuring spectra at 2100 s several samples were photobleached for 5 min either with the full light of a tungsten–halogen lamp or through a 450-nm cut-on filter. In the latter case very little light was absorbed by Cl_2^-. The results of photobleaching are given in Table III. The amount of light incident on the samples during each bleaching was only roughly the same so that differences in the fraction of e_{vis}^- bleached in different samples are not significant. There were indications from repeated bleaching of the same sample with full light that, after 90% of e_{vis}^- had been bleached, the ratio of Cl_2^- bleached to e_{vis}^- bleached $(\Delta G(Cl_2^-)/\Delta G(e_{vis}^-))$ increased with further bleaching. The values of ΔG in Table III were calculated as described above. Essentially the same results were obtained by graphically separating the e_{vis}^- and Cl_2^- bands and equating their decay to the change in the areas under their absorption bands.

9.5 M LiCl/D_2O. The 10^{-7}- and 2100-s spectra are shown in Figure 1, indicating a shift of $\lambda_{max}(e_{vis}^-)$ from 625 to 575 nm. Figure 2 contains the decay curves at 1800, 650, 550, and 350 nm. The "best" value of $G\epsilon_{350}$ at 2100 s is, as discussed above, the ▲ in Figure 2 which is 15% below the solid line. The decay kinetics between 10^{-7} and 10^{-3} s were found to be identical at 1800 and 2300 nm despite the fact that ϵ_{2300} is twice as large as ϵ_{1800}. Hence, no spectral shift is evident for e_{ir}^- during its decay.

Windowless samples avoid both the absorption produced in Suprasil windows and the danger of breaking cells when samples crack. Figure 2 contains the 650-nm decay curve

for windowless samples of 9.5 M LiCl/D$_2$O. It is very similar to the 650-nm decay for the enclosed samples except for a reproducible 4% growth between 10^{-7} and 10^{-5} s. No growth was seen for samples in cells.

Further data on 9.5 M LiCl/D$_2$O is contained in Tables I–III.

6 M LiCl/D$_2$O. As indicated by Figure 1, $\lambda_{max}(e_{vis}^-)$ shifts from 625 to 600 nm between 10^{-7} and 2100 s. Figure 2 illustrates the decays measured at 1800, 650, 550, and 350 nm. The "best" value of $G\epsilon_{350}$, i.e., the ▲, is 5% higher than the solid line. The growth of approximately one-third observed at 650 nm between 10 μs and 0.1 s was reproducible. Further data on 6 M LiCl/D$_2$O is contained in Tables I–III.

Discussion

This study deals mainly with reaction 7, the decay of trapped electrons by reaction with Cl$_2^-$. Ershov and Pikaev[5] found a simultaneous decrease in the ESR signals of trapped electrons and Cl$_2^-$ when an irradiated LiCl glass was bleached with visible light and they postulated reaction 7. The average value of $\Delta G(\text{Cl}_2^-)/\Delta G(e_{vis}^-)$ in Table III is 1.2 for bleaching done with full light and 1.1 when light >450 nm was used. There is very little absorption of light by Cl$_2^-$ above 450 nm. These results are strong evidence for an almost 100% decay of photobleached e_{vis}^- by reaction 7. A value of $\Delta G(\text{Cl}_2^-)/\Delta G(e_{vis}^-) = 1.0$ would indicate that e_{vis}^- and Cl$_2^-$ took part only in reaction 7 and that the correct values of ϵ were used. The possibility that there is no connection at all between the decay of e_{vis}^- and Cl$_2^-$ in unlikely since the results are independent of the value of $G(\text{Cl}_2^-)/G(e_{vis}^-)$ before photobleaching, a value which varied by a factor of 3.5 over the range of glasses used. The slightly higher ratio of $\Delta G(\text{Cl}_2^-)/\Delta G(e_{vis}^-)$ with full light bleaching suggests that Cl$_2^-$ was photoionized by UV light. This agrees with the observation that LiCl glasses irradiated to 200 krd and bleached appeared yellow indicating the presence of chlorine.

We now address the question of whether reaction 7 takes place in the absence of light. First, we examine the changes $\Delta G(\text{Cl}_2^-)$, $\Delta G(e_{vis}^-)$, and $\Delta G(e_{ir}^-)$ which occur during the interval 10^{-7} to 10^{-4} s. The measured changes are given in Table II. This time interval was chosen because it encompasses a measurable decay of Cl$_2^-$ along with a wide variation in the fractional decays of e_{vis}^- and e_{ir}^-. Despite these wide variations, the decays during the interval 10^{-7} to 10^{-4} s can be represented to better than 5% by the same equation for all glasses:

$$\Delta G(\text{Cl}_2^-) = 1.24\Delta G(e_{vis}^-) + 0.11\Delta G(e_{ir}^-) \qquad (9)$$

The factor 0.11 associated with $\Delta G(e_{ir}^-)$ could equally represent reaction of e_{ir}^- with Cl$_2^-$ or conversion of e_{ir}^- into e_{vis}^-.

The conversion of e_{ir}^- to e_{vis}^-

$$e_{ir}^- \rightarrow e_{vis}^-$$
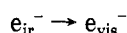
has been observed in ethylene glycol[1] and BeF$_2$[14] glasses. We now suggest its occurrence in LiCl glasses, based on the small growth at 650 nm from 10^{-7} to 10^{-5} s in windowless 9.5 M LiCl and the growth at 650 nm from 10^{-4} to 10^{-1} s in 6 M LiCl. Both these growths take place during an interval when substantial amounts of e_{ir}^- decay. It is unlikely that the growths are due to a spectral shift within the visible band itself. In the case of 6 M LiCl the growth at 650 nm only occurs toward the end of the e_{ir}^- lifetime. Presumably conversion at earlier times in 6 M LiCl is masked by the rapid concomitant decay of e_{vis}^-. A similar growth in e_{vis}^- has been reported for 2.5 M MgCl$_2$ glass.[1] Given the noticeable decay at 650 nm between 10^{-7} and

10^{-5} s in both 6 and 12 M LiCl it now seems that the lack of decay in 9.5 M LiCl contained in a cell may be due to a compensatory conversion of e_{ir}^- into e_{vis}^-. This is suggested by the growth of e_{vis}^- found in windowless 9.5 M LiCl glass. The windowless method used nonwettable removeable plates when mixing glasses. When samples were formed inside wettable Suprasil cells the glasses were found to be very strongly attached to the cell walls. The windowless samples were probably less strained than their counterparts in the cells and this may have caused a slightly slower initial decay of e_{vis}^-. Different methods of making ethanol glasses have been shown to result in different spectra at 4.2 K.[16] We calculate 6% conversion of e_{ir}^- to e_{vis}^- in both 9.5 and 6 M LiCl during the interval in which the absorption at 650 nm grew by assuming that no decay of e_{vis}^- took place during that interval. This is obviously a lower limit for the conversion reaction.

We may say that the measured value, $\Delta G(e_{vis}^-)$, equals the total amount of e_{vis}^- which has reacted, $\Delta G_{abs}(e_{vis}^-)$, less the conversion of e_{ir}^- into e_{vis}^-. If we assume that 6% of the decay of e_{ir}^- between 10^{-7} and 10^{-4} s is due to conversion into e_{vis}^- we can rewrite eq 9 in the form

$$\Delta G(\text{Cl}_2^-) = 1.20\Delta G_{abs}(e_{vis}^-) + 0.04\Delta G(e_{ir}^-)$$

If a 9% conversion were assumed (6% is a lower limit) the equation becomes

$$\Delta G(\text{Cl}_2^-) = 1.23\Delta G_{abs}(e_{vis}^-) \qquad (10)$$

which is obeyed within 5% at all three LiCl concentrations. We conclude that, between 10^{-7} and 10^{-4} s, e_{vis}^- decays in the dark almost entirely by reaction with Cl$_2^-$ just as it does when photobleached. It is equally probable that little or no e_{ir}^- reacts with Cl$_2^-$. This difference between the decay modes of e_{ir}^- and e_{vis}^- is consistent with the fact that e_{ir}^- decay leads to light emission whereas no emission is observed which correlates with the decay of e_{vis}^-.[1] It was earlier concluded that reaction of e_{ir}^- with OD radicals (reaction 8) was the most likely source of emission.[1]

The fact that the factor associated with $G_{abs}(e_{vis}^-)$ in eq 10 is slightly greater than 1.0 is reminiscent of the photobleaching results in Table III. Once again, the possibility arises that the extinction coefficients used in the calculations are in error. However, the measurements in the interval 10^{-4} to 2100 s suggest the alternate possibility that a reaction other than (7) may account for some of the decay of Cl$_2^-$.

Equation 10 represents only 44 (±9)% of $\Delta G(\text{Cl}_2^-)$ during the interval 10^{-4} to 2100 s. It appears that a reaction other than (7) accounts for a large fraction of the Cl$_2^-$ decay over this time interval. This reaction might also account for a small fraction of the Cl$_2^-$ decay during the interval 10^{-7} to 10^{-4} s, thereby accounting for a factor >1.0 associated with $\Delta G_{abs}(e_{vis}^-)$ in eq 10. The nature of this additional reaction of Cl$_2^-$ is unknown. Presumably the diffusion constant of Cl$_2^-$ at 72 K is so low as to preclude reactions other than with species present in high concentration or species formed in the same spur as Cl$_2^-$. Many of the rate constants for reactions of Cl$_2^-$ in aqueous solution have been determined.[13,17-19] The formation of Cl$_2^-$ in aqueous solution is complex and not well understood[19,20] so that a detailed knowledge of the other components of the spur is not possible.

A very obvious concern is that the species absorbing in the UV might be partly ClOD$^-$ rather than completely Cl$_2^-$. $G\epsilon_{max}(\text{ClOD}^-)$ is likely to be less than half the value of $G\epsilon_{max}(\text{Cl}_2^-)$ since $G\epsilon_{max}(\text{ClOH}^-) = 0.37 \times 10^{-4}$.[13] The calculated value of $G(\text{Cl}_2^-)$ in 12 M LiCl (Table I) is close to the maximum expected value of 4.0[18] so that the presence

of substantial amounts of $ClOD^-$ is unlikely. The presence of $ClOD^-$ in 6 M LiCl cannot be discounted.

Experiments on LiCl glasses at 76 K led to the suggestion that e_{ir}^- is probably trapped in an amorphous "free" water environment whereas e_{vis}^- is mainly associated with water bound to Li^+.[2] This description of the e_{ir}^- trap seemed less likely when values of $G(e_{ir}^-) > 1.2$ were found by pulse radiolysis for 12 and 14 M LiCl[3,4] at 6 K. At such high concentrations of LiCl very little "free" water is expected because of the presence of $Li(H_2O)_4^+$ and $Cl(H_2O)_6^-$ units in $LiCl/H_2O$ glasses.[20] The results of the present study suggest that e_{vis}^- is trapped in the vicinity of Cl_2^- and, hence, in water initially associated with Cl^-. This probably simply means that e_{vis}^- is located in the region of the solvated Li^+ and Cl^- ions.[21] On the other hand, e_{ir}^- appears not to be trapped in the vicinity of Cl_2^- which may mean that e_{ir}^- is in a region of free water or simply that it is remote from Cl_2^-.

The formation of Cl_2^- in aqueous 1–5 M NaCl was found by picosecond pulse radiolysis to be complex but most consistent with Cl atom formation by reaction of H_2O^+ (i.e., reaction 1). The formation of Cl_2^- seemed too fast to involve the normal diffusion processes expected for OH reactions (i.e., reaction 3).[18] As found with concentrated NaCl solutions, we find $G(Cl_2^-)$ at 100 ns in 12 M LiCl to be close to the value of 4.0 expected for G(initial ionization). Since $G(e_{ir}^- + e_{vis}^-) = 1.95$ at 100 ns a decay of $G(e^-) = 2.05$ must have already occurred and apparently not mainly by reaction with Cl_2^-. A material balance dictates that much of the Cl_2^- in LiCl glasses is produced via reactions 2, 3, and 4. In this mechanism D_3O^+ and OD are formed which can also react with electrons.

Conclusions

In LiCl glasses at 76 K and after 100 ns, over a wide range of LiCl concentrations, e_{vis}^- decays almost entirely by reaction with Cl_2^-, both in the absence of light and during photobleaching. On the other hand, reaction with Cl_2^- does not seem to be involved in the decay of e_{ir}^-. Some conversion of e_{ir}^- into e_{vis}^- probably occurs fairly universally

in LiCl glasses although observation of this process is difficult. A considerable fraction of the Cl_2^- decay between 10^{-4} and 2100 s occurs via reactions other than with trapped electrons.

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