Physical and Chemical Processes Accompanying the Dissolution of Irradiated Substances, Studied by Means of Luminescence Measurements

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When certain gamma irradiated substances are dissolved in water, a light emission is observed. Alkali halides seem to be most efficient in this respect. In such systems the light emission is also considerably increased by the addition of certain fluorescent substances to the solvent.

The light emission caused by dissolving irradiated NaCl in a fluorescein solution was studied as a function of the radiation dose in the range $1-10^6$ rad. In contrast to solid state luminescence, for example thermoluminescence from irradiated alkali halides, the relative luminescence yield was found to increase with increasing total dose above around 30 rad.

Substances such as O_2 and NO_3^- as well as reducing agents were found to quench the luminescence in concentration ranges where no effect could be observed on the light induced fluorescein fluorescence. On the basis of these results, a hypothetical reaction mechanism has been advanced in good agreement with experimental data.

When ionizing radiation is absorbed by matter both excitation and ionization occur. The excited electron usually returns to the ground state in a very short time and the energy is either emitted as light (fluorescence and phosphorescence) or converted to heat. The electron which escapes from the original atom, leaving behind a positive hole, may be trapped at some defect in the crystal lattice. In ionic crystals (such as alkali halides) this defect usually constitutes an anion vacancy * and the hole is generally represented by a halide atom. The electron can remain in the trap for a long time, depending on circumstances such as the depth of the trap, the temperature, and so forth.

In Fig. 1 a simple energy level diagram is shown.

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* The electron trapped in the anion vacancy is called an F-center.

Fig. 1. Energy level scheme of a crystal lattice containing structural defects; C, conduction band; V, valence band; T, trap; E_A, activation energy; solid arrows, path of ionization; dotted arrows, path of deactivation by heat or light.
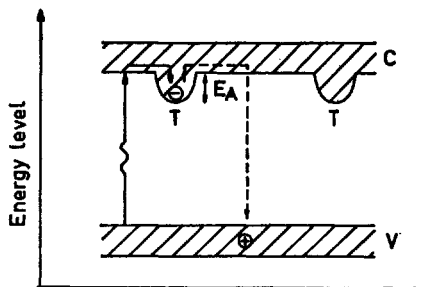
By supplying energy to the crystal, the electron can be lifted to the conduction band, as indicated in the figure, and is then free to recombine with the hole. Alternatively, the electron may be released from the trap, when the irradiated material is dissolved in some suitable solvent.

When the activation energy is supplied as heat or light, the electron is set free and the energy released when the electron combines with the hole is equal to the difference between the energies of the conduction band and of the valence band. In the process induced by dissolution, the picture will be a little different due to the fact that the electron will probably never be free. The bonds between the electron and the surrounding positive ions in the crystal lattice are broken by the formation of ion-dipole bonds between positive ions and solvent molecules and between electrons and the solvent. (This process is similar to that occurring when NaCl is dissolved in water, and probably when Na-atoms react with water). The recombinations will occur between solvated entities and consequently the energy released in these recombination processes will be different from that obtained by recombinations in the solid state.

In a previous report [1] we described light emission found when irradiated organic substances were dissolved in water. Westermark [2,3] described the same process for irradiated alkali halides and organic compounds. The same author also found that the light emission could be increased by a factor of one thousand by the addition of certain fluorescent substances to the solvent. The light emission was proportional to the dose up to about 10 Mrad where a slightly inclining plateau was reached.

However, when the relationship between the dose and the light emission for gamma irradiated NaCl dissolved in various fluorescent solutions was investigated down to very low doses, we found the light emission per rad to decrease as the total dose decreased.

It was also observed that a number of substances, such as O_2, NO_3^- and SO_3^{2-}, quenched the luminescence obtained by dissolution of irradiated NaCl in a fluorescein solution. However, at the same concentrations, these quenchers had no effect on the UV- and visible light induced fluorescein luminescenec.

EXPERIMENTAL

Apparatus. Fig. 2 shows: a) a schematic diagram of the luminescence measuring device. b) Photomultiplier (PM) tube, sample holder and light guide.
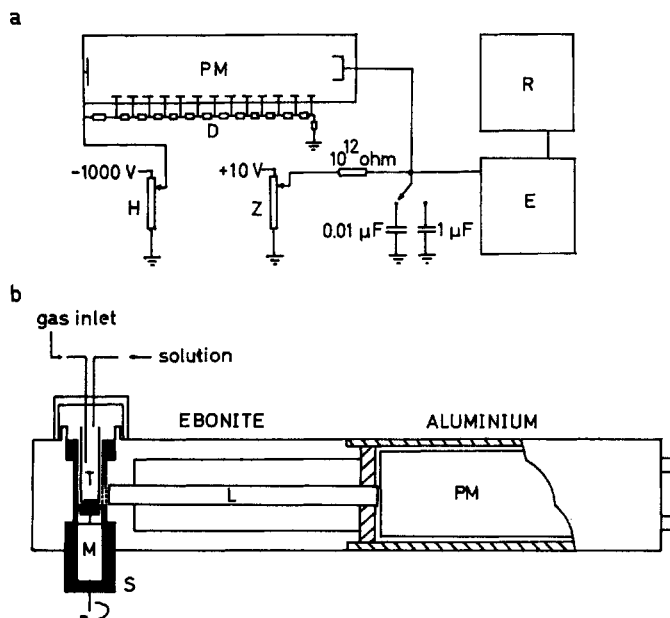

Fig. 2. a) Luminescence measuring device; PM, photomultiplier tube (EMI 6256 S); H, high voltage supply; Z, zero setting; D, dynode resistance chain; E, electrometer (Keithley 600 A); R, recorder (Moseley Autograph 680); b) PM, photomultiplier tube; M, magnet stirrer; S, sample holder; T, test tube with sample and magnet; L, light guide (plexiglas).

The light path from the sample to the PM tube is opened and closed by rotating the sample holder through 180°, as indicated by the arrow in Fig. 2 b. When emission spectra are recorded, a Bausch & Lomb grating monochromator is inserted between the sample holder and the PM tube. In this arrangement, a quartz lens system is introduced in the position of the light quide. The PM tube may be cooled by solid carbon dioxide, and the dark current is hereby reduced by a factor of 10. Generally, cooling is necessary only when the monochromator is used.

In this equipment an EMI 6256 S-type PM tube was used. Tubes of this type are specially processed to obtain a low dark current. The manufacturer claims that the dark current due to thermal release of electrons from the cathode in the S-tube is reduced at least 10 times with only a small loss in quantum efficiency in the red region of the spectrum, as compared to the usual A and B type PM-tubes. We found that all S-type PM-tubes used in our laboratory had at least 50 times lower dark current than the ordinary A-type, and in the range of wavelengths studied (250—600 mμ) the spectral response curves for the two types of tubes were identical.

Calibration of absolute counting efficiency. The quantum efficiency of the light measuring device was obtained by using Cherenkov light from ^{32}P-decay in water. This light was filtered by a Baltzer's Broad Band Interference Filter (Filtraflex K2) with the maximum transmission at 440 mμ. According to Anderson and Belcher,[4] 51 photons

in the range $300-700$ mμ are emitted on an average from one ^{32}P-decay. It was calculated that 6.9 % of the Cherenkov radiation is transmitted through the above mentioned filter.

As a stable substandard light source in all measurements we used a mixture of 0.005 ml tritiated water (0.45 mC ^{3}H), 0.095 ml absolute ethanol, and 0.9 ml toluene containing 3 g PPO and 0.03 g POPOP per litre. This solution was found to emit 2.65×10^8 photons per sec (16 photons per tritium β-particle), the maximum emission being at 420 mμ.

Irradiations. The material was irradiated in a Picker ^{60}Co-source, type Hot Pot containing about 1500 C ^{60}Co, and giving a dose rate of 5000 R/min. This dose rate could be reduced to 800 R/min by lead shielding of the samples in the irradiation chamber. With this arrangement the minimum dose which could be obtained in this equipment was 30 rad.

Irradiations with lower doses were done at different distances from a small ^{60}Co-source giving a dose rate of 1.6 Rhm.

The dosimetry of the Picker Hot Pot has been desribed earlier.[5]

The 1 C ^{60}Co-source was calibrated by using the Fricke dosimeter at 10 cm and 20 cm distance from the radioactive material; at greater distances another, more sensitive, chemical dosimeter system [6] was used.

Determination of F-centers. It is well known that the origin of the material has a great influence on the number of F-centers produced per dose unit as well as on the maximum number of F-centers which can be obtained.[7],[8]

When testing coarse NaCl and triturated NaCl, it was found that in the latter case a higher light yield was obtained per unit weight of the material dissolved.

Because of an extensive light scattering it is usually not possible to measure optical density of powders in an ordinary spectrophotometer. However, by using a Zeiss RPQ20A spectrophotometer equipped with a Zeiss re-emission unit which measures light from the sample over a 180° space angle, it was possible to determine the number of F-centers in both types of samples. It was found that in the pulverized NaCl, a higher initial yield of F-centers as well as lesser saturation effects were obtained. (Fig. 3). The limiting
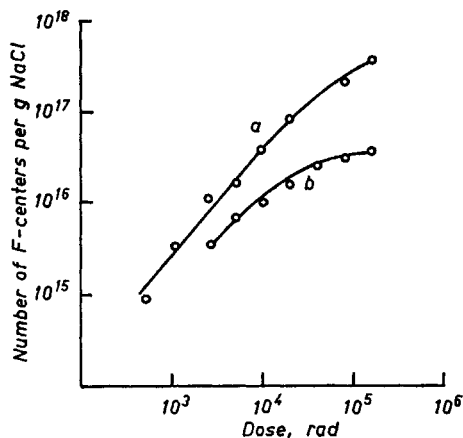
Fig. 3. Number of F-centers per gram of NaCl as a function of the dose for a) a finely pulverized sample, and b) a coarse sample of NaCl. Optical density measured at 460 mμ. For calculation of number of F-centers see Przibram.[7]

factor in the production of F-centers seems to be the existing amount of crystal defects, for example anion vacancies.[8] Defects of this type are obviously introduced by a procedure as simple as grinding the NaCl crystals.

Dissolution procedure. The irradiated material was placed in a test tube in the sample holder. The solvent was injected through a 1 mm cannula. If coarse NaCl was used, the dissolution process was speeded up by stirring (Fig. 2 b). The magnets were tiny polythene-covered pieces of iron nails. The sample and the test tube could be flushed with N_2 when air-free conditions were required.

The mechanical treatment of the NaCl crystals gave the same effect as radiation, the luminescence obtained by dissolution of unirradiated but ground material being equal to that emitted from NaCl irradiated with a few rad. By heating to about 400°C for some minutes this effect vanished. Another luminescence phenomenon was also observed to accompany the dissolution of unirradiated material. After injection of the fluorescein solution a slowly increasing luminescence appeared. However, this luminescence could easily be distinguished from the fast light flash from irradiated material.

Immediately after the irradiation the NaCl is strongly phosphorescent and this luminescence had a disturbing influence on the zero setting of the light measuring instrument during the first hours after the irradiation. To avoid this complication all samples were stored at least one day before the dissolution experiments were performed.

The use of finely ground material caused some difficulties as NaCl (Merck *pro analysi*) is slightly hygroscopic. Although parallel tests showed good reproducibility when performed simultaneously, the light yield was found to decrease once the container had been kept open. This problem may be solved by using material of highest purity.

The integrated light emission from dissolution of irradiated material was measured as the voltage of a condenser (1 μF or 0.01 μF) charged by the PM-tube current. The duration of the light flash from dissolving triturated NaCl was determined by means of an oscilloscope to about 100 msec.

RESULTS AND DISCUSSION

When NaCl irradiated with doses ranging from a few rad up to one Mrad, was dissolved in a solution containing a suitable fluorescent substance, it was observed that the light yield per unit dose increased with an increasing total dose. (The same result was obtained for irradiated NaF.) This effect is shown in Fig. 4 where the light yield per unit dose is represented as a function of the total dose when 50 mg of irradiated NaCl are dissolved in 1 ml 10^{-4} M air-equilibrated fluorescein solution at pH 7. This fluorescein concentration was found to give an optimum light yield, as shown in Fig. 5. Other fluorescent substances such as Tl^+ and Rhodamine B give curves of the same general type as shown in Figs. 4 and 5, the main difference being a lower absolute light yield.

The first part of the curve in Fig. 4 shows a linear relationship between light emission and total dose. Between 30 and 1000 rad, the light emission is approximately proportional to the square of the dose and above this dose region the dose dependence seems to be logarithmic. The decrease in light
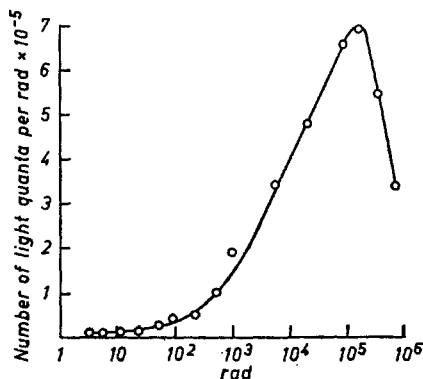
Fig. 4. Luminescence yield per unit dose as a function of the dose in presence of fluorescein.
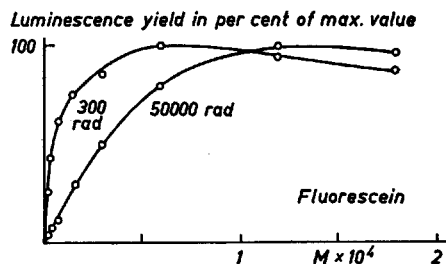
Luminescence yield in per cent of max. value

Fig. 5. Luminescence yield in per cent of maximum value as a function of the fluorescein concentration, given for two different doses.

yield per rad, observed at the highest doses, can probably be attributed to a saturation in the formation of F-centers. This effect depends on the type and pretreatment of the material used.

IDENTITY OF THE PRIMARY SPECIES FORMED BY DISSOLUTION

In the hypothetical reaction models set up in order to explain the non-linear relationship between light yield and dose, hydrated chlorine atoms and electrons are assumed to be the primary agents formed upon dissolution. When irradiated NaCl is dissolved in water, Cl_2 is formed and the solution becomes alkaline.[9] The production of Cl_2 upon dissolution can readily be explained by the presence of Cl atoms in the irradiated crystal. The OH^- might be formed by the reaction of water with free sodium [9] or, more probably, by the decay of an electron-water complex.[10]

If the F-center electron were bound exclusively to one sodium ion in the crystal lattice, it could be expected that all sodium halides have similar absorption spectra and that the trap depth in a sodium halide crystal should be approximately equal to the ionization potential of sodium. This is not the case; rather, the F-center electron is bound equally firmly to the six surrounding sodium ions.[11]

Thus it seems extremely unlikely that, upon dissolution of the crystal, an F-center electron would first be captured by one of the surrounding sodium ions and then become hydrated in the rapid reaction with water molecules.

Irradiated NaCl dissolved in pure water emits light in the range 350—550 mμ. The absorption spectra for halide ions have been determined in the gas phase,[12] and maxima have been found in the wavelength range of 290—450 mμ. From these data, the electron affinities for F, Cl, Br, and I, have been determined to be 3.35, 3.60, 3.36, and 3.06 eV,[12] respectively. These values are well in accordance with the observed maxima in the emitted luminescence.

It is highly probable that the release of energy, observed as luminescence when irradiated NaCl is dissolved in water or fluorescein, originates from the recombination of $Cl\cdot$ and e^- (or e_{aq}^-) giving rise to an excited Cl ion, (denoted Cl^-* in the following). Although $Cl\cdot$, e_{aq}^-, and Cl^-* have not been positively identified, these designations will be used in the following text.

REACTION MECHANISMS

When the Cl atoms and electrons are set free by the dissolution of the irradiated material, they begin to participate in chemical reactions of different types. These reactions will commence as soon as the reactive species are exposed to the solvent and for a short time the e^- and Cl· will exist as partially hydrated forms in the crystal-liquid interphase.

This infers that we might distinguish between two types of reactions: one reaction type applying to the presence of both participants in solution, the other type being realized when *one* of the participants remains in the crystal lattice — an interphase reaction. We may suppose that the recombination between an electron and a Cl atom gives rise to an electronically excited state $Cl^-{}^*$, the energy of which can be transferred to a fluorescent molecule in the solution and finally emitted as a quantum of light. The excitation energy of $Cl^-{}^*$ may also be converted to heat, either by internal conversion or induced by collisions with solute or solvent molecules. Further, it is reasonable to assume that an electronically excited state formed in the interphase will be more protected in respect to encounter deactivation than an excited state in solution. This will result in a longer life time of the excited state compared to that obtained in solution, *i.e.* a higher probability of an energy transfer to the molecule capable of fluorescence.

The relative luminescence yield, then, must increase as the relative proportion of interphase reactions increases.

Interphase model. The interphase reactions will take place only in a limited space, a "cage", the size of which will be defined as the space occupied by the partially hydrated electrons and Cl atoms in the crystal surface and the fully hydrated species in the solution sufficiently close to the crystal surface to have a fair chance of reacting with an electron or a Cl atom, respectively, in the interphase. Once an e_{aq}^- or Cl· escapes from the cage by diffusion or is removed by the stirring process, it has little chance to return to the cage and consequently it will sooner or later react in the solution outside the cage.

The size of the cage may also be defined in terms of time. The hydration of the NaCl crystal takes place at a certain, constant rate, which will determine the life time of the partially hydrated species which are available for interphase reactions.

We may then proceed to discuss the relative proportion of interphase recombinations, recombinations between fully hydrated species taking place within the cage, and those taking place outside the cage, respectively, during a period of time corresponding to the hydration time for one crystal layer of NaCl as a function of the dose, *i.e.* as a function of the concentrations of Cl· and e^-.

The luminescence yield (Y_t) obtained from recombinations of Cl· and e^- derived from one hydrated "layer" of NaCl and the solvent part of the cage will be expressed by

$$Y_t = Q_j(R_s q_s + R_{sc} q_{sc} + R_i q_i) \tag{1}$$

where R_i, R_{sc}, and R_s are the number of recombinations occurring in the interphase, in the solvent part of the cage, and in the solution outside the

cage, respectively, expressed in moles per litre. q_i, q_{sc}, and q_s are the quantum efficiencies of energy transfer to a fluorescent molecule from an excited state formed in the interphase, in the solvent part of the cage, and in the solution outside the cage, respectively, and Q_f represents the quantum efficiency for light emission from the excited fluorescent molecule.

Other types of recombinations will also occur, such as the dimerization of Cl atoms and the reaction $e_{aq}^- + e_{aq}^- = H_2 + 2OH^-$, but these will occur at a lower rate [13] and play little role in the luminescent process.

Cl· and e^- are produced in equal quantities by the irradiation of NaCl. If initially $[e_{aq}] = [Cl·] = c_0$ in the space comprising the interphase and the solvent part of the cage, and the recombination rates between Cl· and e_{aq}^- are the same in the interphase and in the solvent part of the cage we obtain the following expressions for the cage reactions:

$$dR_i + dR_{sc} = k\,[e_{aq}^-][Cl·]dt \qquad (2)$$

and

$$dR_i + dR_{sc} = k(c_0 - R_c)^2 dt \qquad (3)$$

where the number of recombinations in the cage
$R_c = R_i + R_{sc}$

If $dR_i + dR_{sc} = dR_c$ and $q_c = (R_i q_i + R_{sc} q_{sc})/(R_i + R_{sc})$ (mean quantum efficiency for energy transfer from an excited state in the cage) we obtain by substitution into (1)

$$Y_t = Q_f \left(q_s R_s + q_c \int_0^t dR_c \right) \qquad (4)$$

By solving (3) and substituting into (4) we obtain

$$Y_t = Q_f \left(q_s R_s + q_c \frac{ktc_0^2}{1 + ktc_0} \right) \qquad (5)$$

The total yield for the entire dissolution of a constant amount of NaCl is given by the expression

$$Y_{tot} = \sum_{m=1}^n Y_{t_m}$$

where n is the number of intervals t from the beginning to the end of the dissolution.

For the numerical evaluation of eqn. (5) the following values of constants and approximations are introduced.

1. The concentrations of Cl· and e_{aq}^- are assumed to be in proportion to the F-centers in the crystal considering a saturated NaCl solution in the cage.

2. The integration interval, t, is a function of the hydration rate of the crystal, and will be equal to the mean time an electron or a Cl atom remain in the interphase, during which they are available for reactions with solute molecules. The integration time may thus be set equal to the hydration time, t_h, for one layer of Na$^+$ and Cl$^-$ in the crystal lattice. This hydration time was obtained experimentally by measuring the dissolution rate of a NaCl crystal of known

size under vigorous stirring, and was found to be approximately equal to 2×10^{-6} sec.

3. The rate constant for recombination between e_{aq}^{-} and Cl· has not been determined, but such rate constants for similar reactions are given by Hart et al.[13] Schwarz,[14] and Keene.[10] From these data a value of 2×10^{10} M^{-1} sec^{-1} appears to be reasonable.

4. For a comparison between the experimental data obtained, and the theoretical curve derived from (5) only the relative values of q_c and q_s need to be known.

The maximum and minimum luminescence yields in Fig. 4 represent maximum and minimum numbers of interphase reactions, respectively. From this figure the ratio of q_c/q_s is estimated to be 120, when correction is made for saturation in F-center formation. But $R_s = c_0 - R_c$, and by substitution we obtain

$$Y_{\text{tot}} = nQ_f \; q_s \left(c_0 - \frac{ktc_0^2}{1 + ktc_0} + 120 \; \frac{ktc_0^2}{1 + ktc_0} \right) \tag{6}$$

and by inserting $k = 2 \times 10^{10}$ and $t = 2 \times 10^{-6}$ we obtain

$$Y_{\text{tot}} = nQ_f \; q_s c_0 \; \frac{120c_0 + 2.5 \times 10^{-5}}{c_0 + 2.5 \times 10^{-5}} \tag{7}$$

In Fig. 6a Y_{tot} per unit of conc. is plotted as a function of c_0 (solid line). The circles represent experimental data.

Although the correlation is not perfect, one may conclude that in general, the concept of competition between recombination reactions with different quantum efficiencies for luminescence is correct. It is also possible to obtain a better agreement between the experimental data and the theoretical curve by adjusting the different constants, but, essentially, this will hardly supply any new information as long as certain problems concerning the experimental procedure remain unsolved.

These problems can be summarized as follows. As mentioned above, a higher yield of F-centers was obtained by irradiation of the finely ground NaCl, probably due to the introduction of structural defects in the surface of the crystals. Thus an appreciable fraction of the "surplus" F-centers obtained in the pulverized material may be localized to the surface of the crystals. This assumption was supported by the following observations. When fluorescein solution was added *slowly* to the irradiated NaCl crystals, a considerable part of the material remained undissolved. In spite of this, the integrated light yield was not much less than that observed when the NaCl was dissolved completely. These surface-localized F-centers will evidently give a higher local "effective" concentration than that calculated from the mean F-center concentrations.

The slight discontinuity observed in the experimental curve in the middle of the dose range scale may be ascribed to a dose dependence of the optimum fluorescein concentration (Fig. 5). Thus, in practice, it may be difficult to obtain the expected maximum luminescence yield at the higher doses. However,

within a narrow range of doses the theoretical curve can be exactly adjusted to experimental data as shown in Fig. 6 b.

The hypothetical interphase reaction is certainly an oversimplification as no side reactions are considered. Attention must also be paid to the type of energy transfer mechanism. The excited molecules in the interphase are assumed to be protected from collisions with solvent and solute molecules, causing radiationless deactivation. If one assumes the energy transfer to occur in encounter processes, it follows that collisions with fluorescent molecules would be prevented to the same extent. This implies that the transfer is probably realized by a long range transfer process, for example by resonance transfer, which might explain the great difference between q_c and q_s. It is also possible that the Cl^-* formed in the interphase is different from that formed in solution.

Solvent model. It is also possible to deduce a reaction model which is also based on the existence of a cage, but where it is not necessary to consider the mechanisms of energy transfer. We may assume that the recombination between e_{aq}^- and $Cl\cdot$ gives an excited state with a certain quantum efficiency for energy transfer to a fluorescent molecule, and we need not consider if the recombination takes place as an interphase recombination or in the solution. The first order decay of e_{aq}^- with a half time of about 2.5×10^{-5} sec,[10] and which gives $H\cdot$ and OH^-, will compete with this recombination. Reactions with oxygen and impurities have also to be considered.

When $Cl\cdot$ and e_{aq}^- are removed from the cage by the stirring process, an extensive dilution of e_{aq}^- and $Cl\cdot$ is provoked, and relatively to the decay of e_{aq}^-, which is not affected by dilution, the primary reactions between $Cl\cdot$ and e_{aq}^- will hereby be considerably reduced. Consequently, recombinations between $H\cdot$ and $Cl\cdot$ outside the cage will constitute the major reaction pathway. As explained by the Franck-Condon principle,[15] recombinations between two atoms will have less chance than the recombination between an electron and an atom to create electronically excited states.

Fig. 6. Luminescence yield per unit of concentration as a function of the effective concentration of e_{aq}^- ($= Cl\cdot$) corresponding to the volume of saturated $NaCl$ formed upon dissolution of the crystals. Solid line represents theoretical curve and circles experimental data.
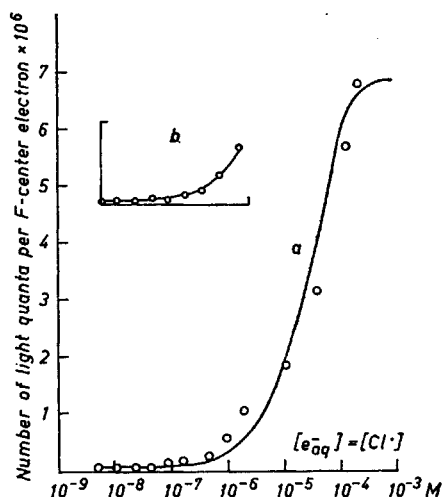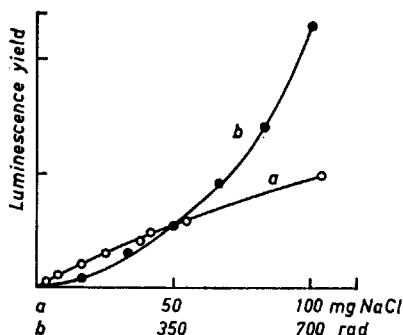
Fig. 7. The effect on the luminescence observed when the concentration of e_{aq}^- (= Cl·) is increased either by a) increasing the amount of irradiated NaCl dissolved at a constant dose (350 rad), or by b) increasing the dose using a constant amount of NaCl (50 mg). The same results are obtained independent of if 0.5, 1, or 2 ml fluorescein solution is injected.

We may now, in eqn. (1) define R_s as the recombination between H· and Cl·, and q_s as the quantum efficiency for the *formation and transfer* of electronic excitation from the recombination compound product of H· and Cl·, and we will obtain the same expression for this reaction model as we obtained for the interphase model. The constants will be the same, except for the hydration time, t_h, which will not be restricted to the period of time during which Cl· and e_{aq}^- are available for an interphase reaction, but which must be extended to the time Cl· and e_{aq}^- remain in the cage.

The maximum dilution factor which could be obtained can be calculated from the amount of material dissolved in a certain volume, from the hydration time, and from the duration of the light flash obtained by dissolving the irradiated material. For 50 mg NaCl dissolved in 1 ml fluorescein solution, assuming $t_h = 2 \times 10^{-6}$ sec and the duration of the light flash to be 0.1 sec, a dilution factor of approximately 3×10^5 is obtained. From Figs. 3 and 6 we can see that a dilution by a factor of 1000 is sufficient, within the concentration range studied, to obtain a change from the maximum luminescence yield to the minimum one, *i.e.* to reduce the concentration of e_{aq}^- and Cl· to such an extent that primary recombinations between e_{aq}^- and Cl· will be of no importance compared to secondary reactions.

The concept of the existence of a cage and the validity of the dilution effect are supported by the experimental results shown in Fig. 7, in which the luminescence yield is plotted as a function of the amount of material dissolved per unit volume of solution. The NaCl is irradiated with a dose in the exponential range of the luminescence yield—dose curve (Fig. 4).

Provided that no cage exists, and that the reacting species are homogeneously distributed in the reaction volume, interaction between Cl· and e_{aq}^- in the solvent may be expected to result in the same effect when the concentration of recombinants is increased either by increasing the relative amount of material dissolved or by increasing the dose given to a fixed amount of NaCl.

QUENCHING OF THE LUMINESCENCE INDUCED BY DISSOLUTION OF IRRADIATED MATERIAL

Organic fluorescent substances are comparatively insensitive towards quenching agents of different kinds. However, the fluorescein luminescence

induced by dissolution of irradiated NaCl was found to be profoundly influenced by many different agents added at concentrations where the light-induced fluorescein luminescence was not affected. One type of agent included molecules such as O_2, NO_3^-, acetone, and H_3O^+ which are known to be e_{aq}^- scavengers.[13],[14] The oxidized coenzyme, $NADP^+$, was also found to quench the luminescence. The second type of substance may be characterized as reducing agents, such as SO_3^{2-} and NADPH. No strictly quantitative investigations have yet been performed concerning these quenching effects, but it was observed that agents such as O_2 and NO_3^- obviously executed their effect at the same point in the luminescent process. The presence of NO_3^-, for example, in a high concentration reduced the quenching effect of oxygen and *vice versa*. However, when SO_3^{2-} was used the quenching power of oxygen was affected only to a limited extent. These results may indicate that both O_2 and NO_3^- can react with e_{aq}^- (or Cl^-*) while reducing agents may act as $Cl \cdot$ scavengers.

At present no experimental evidence is available in favour of one or the other of the hypothetical mechanisms discussed. It is clear that interphase recombinations occur and that side reactions of different type have to be considered. Therefore it is not possible to decide definitely which mechanism is most important until the energy transfer mechanism has been clarified. Unfortunately the system described in this paper is not truly suitable for distinguishing between long range transfer processes and encounter transfer mechanisms, (*cf.* Förster [16] and Reid [15] concerning different types of energy transfer mechanisms), since several steps are involved in the luminescent process.

However, some preliminary experiments, utilizing the system containing tritiated water and fluorescein, saturated with NaCl, indicate a solution of these problems. This system gave a luminescence yield directly proportional to the ^{3}H-activity. The calculated dose rate from [3]H β-particles corresponded to a concentration of e_{aq}^- and $Cl\cdot$ where recombinations play little role.

From the observation that a considerably higher luminescence yield was obtained in a ^3H_2O-fluorescein-NaCl solution than in the ^3H_2O-fluorescein system without NaCl, it could be concluded that the luminescence was not caused by direct excitation of the fluorescein molecule.[17] This view was further supported by the fact that quenchers such as O_2, NO_3^-, and, to a smaller extent, SO_3^{2-}, had the same quenching effect as observed at dissolution of irradiated NaCl in fluorescein solution. It is thus probable that the luminescence exhibited by the ^3H_2O-fluorescein-NaCl system is derived from the transfer of electronic excitation from an excited Cl ion to fluorescein.

This system will allow a further study of the transfer mechanism as it eliminates the complications induced when the excited Cl ion is formed in a recombination reaction.

The absolute quantum effiency expressed as number of light quanta per recombination of $Cl\cdot$ and e_{aq}^- occurring when irradiated NaCl is dissolved in fluorescein was found to be about 7×10^{-6}.

In the ^3H_2O-fluorescein-NaCl system, assuming a maximum of 3 excitations per ionization to occur,[18] the corresponding value was found to be 3×10^{-4}. It seems that a considerable part of the excitation energy is lost

in the recombination process, and this may indicate that the recombination between Cl atoms and electron-water complexes must be considered intermediate to recombinations between atoms on one hand and between an atom and a free electron on the other, with regard to the ability to form excited states, as mentioned above.

So far only singlet excited states have been considered, but it is possible that recombinations between species where the unpaired electrons have parallel spins, may yield excited triplet states. It has been observed that the luminescence obtained by dissolution of irradiated organic material, where free radicals are produced mostly by homolytic fission, was only increased to a small extent by addition of fluorescent substances.[2] In a system previously described by us, where the recombining entities $CH_3 \cdot$ and $Cl \cdot$ were produced by electrolysis,[19] we find no activation of the luminescence by fluorescent substances such as fluorescein and Rhodamine B. This may be explained by the fact that transitions from excited triplet states to fluorescein or Rhodamine B, where singlet excited states are predominant, are less probable than transitions between excited states with the same multiplicity.[20]

REFERENCES

1. Ahnström, G. and v. Ehrenstein, G. *Acta Chem. Scand.* **13** (1959) 199.
2. Westermark, T. and Grapengiesser, B. *Arkiv Kemi* **17** (1961) 139.
3. Westermark, T. and Grapengiesser, B. *Nature* **188** (1960) 395.
4. Anderson, W. and Belcher, E. H. *Brit. J. Appl. Phys.* **5** (1954) 53.
5. Ahnström, G. and Ehrenberg, L. *Risö Report* **16** (1960) 15.
6. Ahnström, G. and Rosén, C.-G. *Acta Chem. Scand.* **19** (1963) 263.
7. Przibram, K. *Verfärbung und Luminiscenz,* Wien 1953.
8. Rabin, H. and Klick, C. C. *Phys. Rev.* **117** (1960) 1005.
9. Hacskaylo, M., Otterson, D. and Schwed, P. *J. Chem. Phys.* **21** (1953) 1434.
10. Keene, J. P. *Radiation Res.* **22** (1964) 1.
11. Seitz, F. *Revs. Modern Phys.* **26** (1954) 7.
12. Berry, R. S. and Reimann, C. W. *J. Chem. Phys.* **38:2** (1963) 1540.
13. Hart, E. J., Thomas, J. K. and Gordon, S. *Radiation Res. Suppl.* **4** (1964) 74.
14. Schwartz, H. A. *Radiation Res. Suppl.* **4** (1964) 89.
15. Reid, C. *Excited States in Chemistry and Biology,* London 1957, p. 173.
16. Förster, T. *Discussions Faraday Soc.* **27** (1959) 7.
17. Ahnström, G. *Svensk Kem. Tidskr.* **77** (1965). *In print.*
18. Bacq, Z. M. and Alexander, P. *Fundamentals of Radiobiology,* London 1961.
19. Ahnström, G. *Acta Chem. Scand.* **15** (1961) 463.
20. Porter, G. and Wright, M. R. *Discussions Faraday Soc.* **27** (1959) 18.