

Quenching Effect of Oxygen on the Light Emission Produced by Dissolution of Irradiated Sodium Chloride in Water

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Dedicated to Professor *Ole Lamm* on his 60th birthday

Light is emitted when irradiated sodium chloride is dissolved in water. It was shown that oxygen was a quencher. Some ideas were put forward about the mechanism by which the stored energy, represented by the structural defects, is released.

It has been shown that, when solids which have been treated with ionizing radiation are dissolved in liquids, chemical reactions typical for radiation chemistry, *e.g.* the oxidation of Fe^{2+} and I^- (Refs.¹⁻³) apparently occur. Aqueous solutions of dissolved sodium chloride originally containing colour centers have been found to be slightly alkaline⁴⁻⁶. Hydrogen is evolved on dissolution³. Light emission is produced when irradiated solids, organic as well as inorganic, are dissolved in certain solvents with or without added solute^{1,8-10}. With water, a small but readily observed light pulse was obtained when irradiated (some Mrads) NaCl was used⁹.

The influence of dissolved gases on the light emission has not been investigated, and the water used in the experiments hitherto has not been air-free. The mechanism by which the stored energy, formally represented by the structural defects at the F- and V-centers, is released upon dissolving, for example, NaCl in water is unknown. If we assume that the released energy acts radiometrically the presence of oxygen in the water may be supposed to interfere in some way. Oxygen, having a biradical character, exhibits well established effects in radiation and photochemistry. An examination of the effects of dissolved gases on the light emission produced upon dissolution of irradiated NaCl in water has therefore been carried out.

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EXPERIMENTAL

From the laboratory supply of distilled water, an alkaline potassium permanganate solution was made and distilled. An acidic potassium bichromate solution produced using the water thus obtained was distilled in a carbon dioxide-free atmosphere. The distillation product obtained was distilled once more and finally in a two-step bidistillation quartz apparatus (Heraeus Quarzschmelze G.m.b.H., Hanau, Model Bi 3) where it was de-aerated to a considerable extent. The water was collected in a flask and saturated with nitrogen.

The fine-grained NaCl used had been given a dose of 5 Mrads by ^{60}Co γ -rays at room temperature and then stored dry and dark in a refrigerator (-25°C). The gases examined (oxygen, nitrogen and hydrogen) were of technical quality. The nitrogen was freed from oxygen by passing the gas through two copper columns kept at about 170°C . The packing material was prepared from sintered copper oxide reduced by flushing with hydrogen to a red colour. The gases were freed from carbon dioxide by means of an Ascarite filter.

The emission of light was observed with the photomultiplier arrangement described in Ref.⁹ The integrated area of the light pulse gives an estimate of the stored energy transformed into light. (Due regard of course has to be taken to the spectral response of the photocathode.)

The irradiated NaCl (10 mg, 5 Mrads) was poured into the water (5 ml) which was contained in a quartz glass vessel placed at the top of the photomultiplier tube. The gas atmosphere in the space above the tube was varied. To make sure that the water was of the same quality in all measurements, nitrogen-saturated water was first used. The nitrogen was then replaced by air, freed from CO_2 , by bubbling the gas directly through the water. Finally measurements were carried out with the water saturated with oxygen.

RESULTS AND DISCUSSION

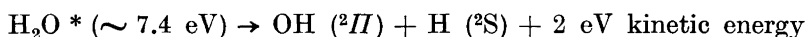
Although the reproducibility of the light pulse areas was not good, it was evident that the presence of oxygen in the water reduced the light emission considerably. Thus water saturated with nitrogen gave light pulses with areas 10–15 times larger than those for oxygen-saturated water. The luminescence from more or less degassed water as well as from hydrogen-saturated water was of the same magnitude as that from the nitrogen-saturated water. Saturation with air reduced the light emission to about 1/4 of that of the nitrogen-saturated water. When NaCl of the same quality but unirradiated was tested, no light emission at all could be detected.

The existence of hydroperoxide in solutions saturated with NaCl which had been previously dosed with 50 Mrads has been investigated but with negative results. Spectrometry in the visible (titanium reagent) and ultra-violet regions has been carried out. The dissolution of NaCl in the presence of benzene in order to get phenol has also been examined. No phenol was found with the ultraviolet spectrometer (Beckman Model DK-2). The concentration of H_2O_2 and phenol may, however, have been too small to be detected under the conditions used.

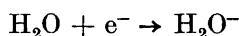
The presence of "free sodium"^{5,6} and "chlorine"⁷ in NaCl containing colour centers has been pointed out. However, the chemical reactions produced when the NaCl crystal dissolves might more appropriately be termed consequences of reactions of electrons and holes rather than of free atoms in the crystal¹¹. The minimum energy necessary to produce colour centers by light in NaCl is about 6 eV (from the absorption spectrum of pure NaCl). This is also stated to be the energy produced by a direct recombination of a free hole

with an electron in an F-center. Thermoluminescence, however, indicates that the energies of the emitted light are about 2.5–3.5 eV¹². These recombination energies may be assumed to be the maximum available for the chemical reactions and the light emission when dissolving the salt. The emission of light probably takes place somewhere in a chain of energy transfer processes and oxygen has a quenching effect. It has been shown that reactions of free radicals produced electrolytically are accompanied by luminescence¹³. An increase in the luminescence was obtained when the water was oxygen-free.

The lowest excited level of water has a broad continuum centered at about 7.4 eV¹⁴. This is a repulsive level and thus there is no, or only very faint, luminescence due to excitation in this band¹⁵. The following reaction takes place:



This reaction will, however, not account for the fates of the electrons and the holes when the crystal dissolves. The largest conceivable recombination energy is not sufficient to promote the reaction. Due to the low energy of the electron it will soon become thermal and most probably be captured by a water molecule according to:

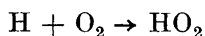


This entity (in solvated form) will then decompose

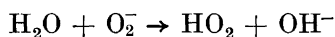
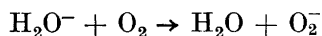
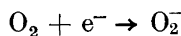


Another and perhaps more likely explanation might be the formation of a self-trapped electron ("polaron")¹⁶.

The presence of oxygen will give rise to other reaction mechanisms. Thus it is likely that available H atoms will react with oxygen to form hydroperoxy radicals:



Oxygen has a high electron affinity and it may also react in other ways:



The reactions stated do not give an explicit explanation of the light emission phenomenon but give some indications of how oxygen can play a role. In the competition between light emission and chemical reactions oxygen may act as a quencher. It would therefore be of interest to examine the effect of oxygen on the chemical dosimeter yield when dissolving irradiated NaCl and on the light yield when using fluorescent solutions. Further information about the nature of the light emitted may be obtained by investigating the spectral distribution of light.

The efficiency for the production of doubly ionized halogens and the conditions for the existence of such entities have been discussed^{17,18}. It was postulated that Cl^+ ions with a high energy content were present. If this is true there is enough energy available to bring about reactions similar to the radiation chemistry of water.

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REFERENCES

1. Westermark, T. *Risö Report* **16** (1960) 28.
2. Westermark, T., Biesèrt, N. and Grapengiesser, B. *Arkiv Kemi* **17** (1961) 151.
3. Burns, W. G. and Williams, T. F. *Nature* **175** (1955) 1043.
4. Kleinschrod, F. G. *Ann. Physik* **27** (1936) 97.
5. HacsKaylo, M. and Groetzinger, G. *Phys. Rev.* **87** (1952) 789.
6. HacsKaylo, M. and Otterson, D. *J. Chem. Phys.* **21** (1953) 552.
7. HacsKaylo, M., Otterson, D. and Schwed, P. *J. Chem. Phys.* **21** (1953) 1434.
8. Ahnström, G. and v. Ehrenstein, G. *Acta Chem. Scand.* **13** (1959) 855.
9. Westermark, T. and Grapengiesser, B. *Nature* **188** (1960) 395.
10. Westermark, T. and Grapengiesser, B. *Arkiv Kemi* **17** (1961) 139.
11. Heal, H. G. *Atomics* **6** (1955) 205, 241.
12. Halperin, A., Kristianpoller, N. and Ben-Zvi, A. *Phys. Rev.* **116** (1959) 1081.
13. Ahnström, G. *Acta Chem. Scand.* **15** (1961) 463.
14. Hochanadel, C. J. *Radiation Chemistry of Water*. Chapter 8 in *Comparative Effects of Radiation* (Editors: Burton, M., Kirby-Smith, J. S. and Magee, J. L.), J. Wiley & Sons Inc., London 1960.
15. Brown, L. O. and Miller, N. *Trans. Faraday Soc.* **51** (1955) 1623.
16. Weiss, J. *Nature* **186** (1960) 751.
17. Howard, R. E. and Smoluchowski, R. *Phys. Rev.* **116** (1959) 314.
18. Howard, R. E., Vosko, S. and Smoluchowski, R. *Phys. Rev.* **122** (1961) 1406.

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