

LETTERS TO THE EDITOR

FLASH PHOTOLYSIS OF SEAWATER

A NUMBER of chemically stable and unstable radiolysis products of seawater are produced during an underwater nuclear explosion. Very little is known, however, about the nature and behaviour of these products^{1,2} especially the primary intermediates formed in the radiochemical act. As a part of our continuing program of work on 'Radiation Chemistry of Seawater', an attempt is made here to identify the transient species formed on flash photolysis of seawater ($3.1 \text{ }^{\circ}\text{Be}$), their decay and reactivity with added solutes of interest.

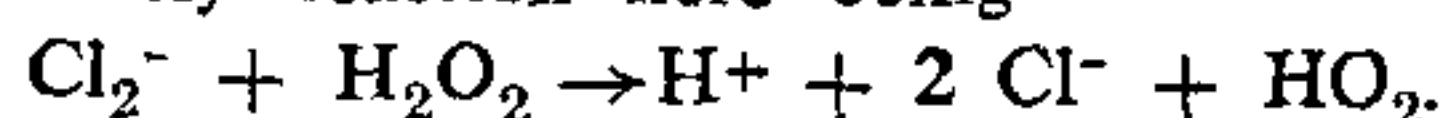
The flash photolysis apparatus used is the same as described by Daniels³. In brief, an intense flash (800 J) is produced by discharging two Sangamo 14 μF rapid discharge capacitors arranged in parallel through the two flash lamps at 8 KV. The quartz lamps are filled with air (6 cm), have a 20 cm interelectrode distance and are enclosed in aluminium box with an internal MgO light reflecting surface. The irradiation vessel made of spectro-sil of 17.2 cm optical path length and 1 cm diameter is placed between the two lamps which are parallel to each other, 8 cm apart. An annular spectro-sil compartment 20 cm long and 1 cm in depth completely surrounds the irradiation vessel and is used to contain chemical optical filter solutions ($2 \cdot 10^{-2} \text{ M}$ acetic acid, cut off 210 nm). The monitoring light source is an osram XDO 450 W Xenon arc lamp. A Hilger medium quartz spectrograph with a scanning photomultiplier attachment (Hamamatsu TVR 136) is used, the output of which is fed *via* a cathode follower to a Tektronix 545 oscilloscope whose traces are photographed on Polaroid 3000 Type 47 and then enlarged to facilitate further analysis.

The transient absorption spectra (O.D. vs λ , nm) obtained on flash photolysis of seawater ($3.1 \text{ }^{\circ}\text{Be}$) showed an absorption maxima at 340 nm, the spectrum was smooth and resembled that of Cl_2^- . The decay of the transient at 340 nm followed a second order and using the extinction coefficient of Cl_2^- , $\epsilon_{340} = 1.25 \times 10^4$ we obtained a $2k = 1.2 \pm 0.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. This is very close to the 2nd order decay of Cl_2^- species $2 \text{ Cl}_2^- \rightarrow \text{Cl}_3^- + \text{Cl}^-$ with $2k = 1.4 \pm 0.1 \times 10^{10}$ as reported in literature⁴. Oxygen has no effect on the decay or its absorption maxima. Studies on the reactivity of

this transient with methanol and H_2O_2 to confirm its identity are being made. In all cases a pseudo first order decay, k' is obtained and this k' when plotted as a function of added solute concentration ($0.1\text{--}2.3 \times 10^{-4} \text{ M}$) gave a straight line and the final k ($\text{Cl}_2^- + \text{S}$) value is calculated from the slope as shown below:

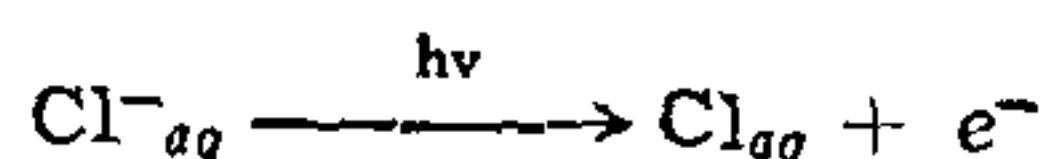
added solute (s)	$k(\text{Cl}_2^- + s)$
CH_3OH (10^{-11} to 10^{-3} M)	$3.2 \pm 0.4 \times 10^7$
H_2O_2 (10^{-2} to 10^{-4} M)	$7.6 \pm 0.4 \times 10^7$

The likely reaction here being

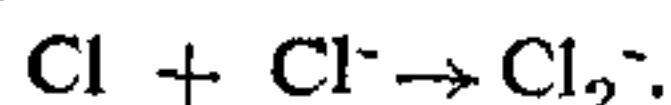


The above values agree well with those reported by Hayon *et al.*⁴. The diminished yield of H_2O_2 per 100 eV [$G(\text{H}_2\text{O}_2)$] on radiolysis of seawater as reported earlier⁵ is now explicable as due to the scavenging of H_2O_2 by Cl_2^- transient formed.

Surprisingly, no complex spectra or evidence for transient species like NO_2 , NO_3 , SO_4^- , CO_3^- (or HCO_3^-), Br_2^- and I_2^- is obtained in seawater although they are present in 10^{-2} to 10^{-4} M . The absence of any other transient absorption maxima in the wavelength region 300–600 nm along with true Cl_2^- decay rate ($2k = 1.2 \pm 0.2 \times 10^{10}$) rules out any possible contribution from other transients. The main photochemical process in seawater seems to be⁷



with Cl atom produced reacting with Cl^- to produce Cl_2^- .



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1. Pestaner, J. F., Report No. U.S.N.R.D.L.T. R.-67-44, 1967.
2. Swallow, A. J., *Nature*, 1969, 222, 369.
3. Daniels, M., U.S.A.E.C. Report No. RC-2014-4, 1969.
4. Langmuir, M. E. and Hayon, E., *J. Phys. Chem.*, 1967, 71, 3808.
5. Parekn, J. M., *Ph.D. Thesis* (unpublished results).