

reaction 1, or by interactions of aldehydes with oxygen or peroxides. Chain propagation is represented by reactions 2a and 2b to emphasize its simplicity. Versions of reactions 2 here involve two acyl radicals IV and three triones. Exchange is effected when reactant IV in 2a is different than the product IV from the succeeding 2b. Reaction 2 is an example of an unusual radical transfer process³ that involves attack upon an internal atom in a molecule and expulsion of a fragment of it. Since triones are the major products, V must be the dominant intermediate or transition state. The small amount of biacetyl from the photolysis of Ia suggests the chain termination reaction 3.

The above equilibria differ from random distribution (Ia,b:IIa,b:IIIa, 2:1:1). Reaction 2b is not expected to be random since small structural differences profoundly affect the fragmentation of *t*-alkoxy radicals.⁴

Similar reactions occur with 1,2-diones. Peroxide- and light-induced reactions of 2,3-butanedione with butanal give some 2,3-hexanedione. Study is continuing to determine if the higher boiling products from photolysis of triones are the hydroxycycloalkanediones anticipated from the photolyses of 1,2-diones to give 2-hydroxycyclobutanones.⁵

Acknowledgment.—We thank the National Institutes of Health for generous support, Grant GM-10702, and the National Science Foundation for the n.m.r. spectrophotometer.

(3) (a) W. A. Pryor and H. Guard, *J. Am. Chem. Soc.*, **86**, 1150 (1964); (b) C. Walling and R. Rabinowitz, *ibid.*, **81**, 1243 (1959).

(4) (a) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padua, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

(5) (a) W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962); (b) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, **14**, 609 (1962).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS 60637

W. H. URRY
MEI-SHU H. PAI
C. Y. CHEN

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Spectrophotometric Detection of Hydrated Electrons in Co⁶⁰ γ -Ray Irradiated Solutions¹

Sir:

In the present letter, we demonstrate the feasibility of direct spectrophotometric determination of e_{aq}^- in Co⁶⁰ γ -ray irradiated solutions. Heretofore, hydrated electrons, e_{aq}^- , have been directly observed only during pulse radiolysis.^{2,3} Extensive use has been made of the intense optical absorption spectrum of the hydrated

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962); J. W. Boag and E. J. Hart, *Nature*, **197**, 45 (1963).

(3) J. P. Keene, *Nature*, **197**, 47 (1963); *Radiation Res.*, **27**, 1 (1964).

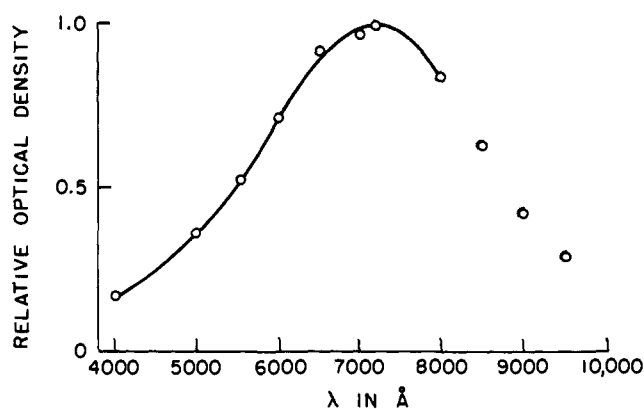


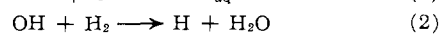
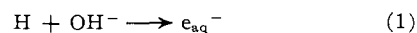
Fig. 1.—Spectrum of the hydrated electron: solid line, pulse radiolysis method, Keene³; circles, present work.

electron to measure absolute rate constants and to demonstrate its formation from hydrogen atoms and photochemically from negative ions.⁴ In the past, such studies have required the use of a linear accelerator but now it is possible to expand work on e_{aq}^- to laboratories having Co⁶⁰ γ -ray or X-ray sources capable of delivering up to 500–1000 rads/sec. available.

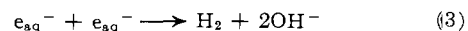
The steady-state concentration of hydrated electrons has been measured in Co⁶⁰ γ -ray irradiated water. We find that the optical density of a 0.001 *N* sodium hydroxide solution saturated with hydrogen increases perceptibly at 7200 Å. upon exposure to γ -rays. The absorption disappears upon removal of the γ -ray source. By measuring the intensity of absorption in the region from 4000 to 9000 Å., we obtain an absorption spectrum identical with that found in the pulse radiolysis of water² (see Fig. 1). When the solution is acidified, no transient absorption is found at 7200 Å. Thus we conclude that this transient species is the hydrated electron.

A water-jacketed, cylindrical irradiation cell, 1 cm. in diameter and 40 cm. in length, provided with supersil end windows, was irradiated in a shielded cave in the chemistry hot laboratory by a 40-cm. long 15,000 c. Co⁶⁰ source. Fluctuations in optical density were minimized by flowing water at constant temperature through the jacket of the cell. The optical absorption of the solution was measured by light from a tungsten filament lamp that passed through the cell into a F 3.5 monochromator and at selected wave lengths into a photocell. Maximum optical density changes of 0.0082 were found at 7200 Å. Under our conditions of irradiation, this optical density change corresponds to an e_{aq}^- concentration of $1.4 \times 10^{-8} M$.

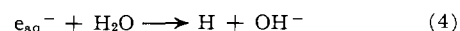
A hydrogen-saturated alkaline solution is an excellent one for studying reactions involving e_{aq}^- . At pH 11, all H atoms and OH radicals formed during irradiation are converted to e_{aq}^- by the following reactions.



The disappearance of e_{aq}^- is primarily by the second-order reaction



since the first-order reaction



(4) Recent summaries are: E. J. Hart, *Science*, **146**, 19 (1964); L. M. Dorfman and M. S. Matheson in "Progress in Reaction Kinetics," Vol. III, G. Porter, Ed., in press.

liberating an H atom regenerates e_{aq}^- by reaction 1.

While no attempt was made to ensure uniform irradiation, the average steady-state (e_{aq}^-)_{ss} concentration is $1.37 \times 10^{-8} M$. This concentration is derived from our optical density of 0.0082, a value of $1.5 \times 10^4 M^{-1} \text{ cm.}^{-1}$ for the molar extinction coefficient of e_{aq}^- and a cell length of 40 cm.

Our demonstration that steady-state concentrations of e_{aq}^- produced by Co^{60} γ -rays may be measured suggests several applications. (1) Accelerators are not required for hydrated electron research. Co^{60} γ -ray sources generating 500-1000 rads/sec. are adequate if multiple-pass irradiation cells are used. (2) Hydrated electron rate constants may be determined by measuring the (e_{aq}^-)_{ss} in the presence of different scavengers. (3) The study of transient spectra such as I_2^- , HO_2 , O_2^- , and other intensely absorbing radicals should be possible. (4) The steady-state measurement of e_{aq}^- offers excellent dosimetric possibilities. The hydrogen saturated alkaline solution can be irradiated indefinitely without change in composition.

Acknowledgment.—The above work was carried out in a remote controlled cave. We gratefully acknowledge the cooperation and technical assistance of Messrs. Harry Youngquist, Howard Harvey, and Joseph Hoe.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS

SHEFFIELD GORDON
EDWIN J. HART

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The Structure of Ethylmagnesium Bromide Dietherate. An X-Ray Diffraction Study¹

Sir:

The structure of the Grignard reagent has been the subject of much speculation and intense study in recent years.^{2,3} In our study the crystal and molecular structures of the ethyl Grignard reagent in diethyl ether have been determined by X-ray diffraction techniques. Since various structures for the Grignard reagent have been proposed based in part or wholly on evidence obtained from experiments on the ethyl Grignard reagent, we feel that our results have a strong bearing on this problem.

Crystals of $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{C}_4\text{H}_{10}\text{O})$ are monoclinic with cell constants $a = 13.18 \pm 0.03$, $b = 10.27 \pm 0.03$, $c = 11.42 \pm 0.03 \text{ \AA.}$, and $\beta = 103.3 \pm 0.3^\circ$. The space group is $P2_1/c$ and there are four molecules per unit cell. The data were recorded photographically at about -75° on the Buerger precession camera using molybdenum radiation. The intensities of 626 independent reflections were judged visually. The bromine and magnesium positions were obtained from a Patterson map, and the remaining positions were determined by a combination of the least-squares and Fourier methods. At this point in the structure determination, the discrepancy factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ is 0.10. The crystallographic details as well

(1) Contribution No. 1603. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958); R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **79**, 347E (1957).

(3) S. Hayes, *Ann. chim. (Paris)*, **8**, 545 (1963); A. Kirrmann, R. Hamelin, and S. Hayes, *Bull. soc. chim. France*, 1395 (1963); R. Hamelin, *ibid.*, 684, 692 (1961).

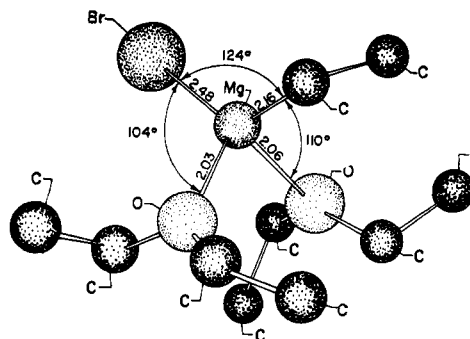
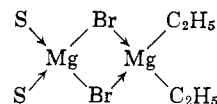


Fig. 1.—The molecular configuration of $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$.

as the results of further refinement will be reported later.

The structure consists of ethylmagnesium bromide monomers (Fig. 1) with the ethyl group, a bromine atom, and two ether molecules forming a distorted tetrahedron about a single magnesium atom. The bond distances to the magnesium atom as well as some representative angles are shown in Fig. 1. The Mg-O bond distance is among the shortest Mg-O distances known. The next shortest Mg-Br distance is 5.81 Å, which is too long to correspond to any sort of chemical bond and rules out all dimeric structures involving bridging bromine atoms. There is essentially trigonal bonding about the oxygen atoms. For a given ether molecule, the distance from the magnesium atom to a plane defined by the methylene carbons and the oxygen atom is about 0.2 Å. The terminal methyl groups on a given ether molecule are nearly opposed to each other.

Previously,³ the favored structure for the ethyl Grignard in the solid state was



where S represents the solvent. It was proposed that the number of molecules of solvent associated with this species is nonintegral and increases with the basicity of the solvent. Also, it was concluded that no species of definite chemical composition existed in the solid state.

In our study, diffraction photographs were taken of many preparations which were purified to various degrees, and in no case was a species obtained different from the monomeric species described. The evidence for the existence of a species of definite chemical composition, namely, the monomeric species, is therefore strong. These results are consistent with those found with the phenyl Grignard reagent, which is also monomeric in the solid state.⁴ Although the evidence presented here does not apply directly to the liquid state, the observations discussed by Stucky and Rundle⁴ in this regard apply equally well here.

In our experiments crystals were grown from the liquid state by slowly cooling the sample with a stream of cold nitrogen gas. This method is similar to that used by Vreugdenhil.⁵ Other authors³ have based their studies on crystals obtained by evaporation of the solvent from a solution of Grignard reagent. This difference may indeed be significant.

(4) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(5) A. D. Vreugdenhil and C. Blomberg, *Rec. trav. chim.*, **82**, 453, 461 (1963).