

Radiation Chemistry—I

Radiation Chemistry

Volume I. Aqueous Media,
Biology,
Dosimetry

An international conference

sponsored by

Argonne National Laboratory

Argonne, Ill.

Aug. 12-15, 1968

Edwin J. Hart

Conference Chairman

ADVANCES IN CHEMISTRY SERIES

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Library of Congress Catalog Card 68-55363

PRINTED IN THE UNITED STATES OF AMERICA

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Exceptional strides are now being made in radiation chemistry although growth has been gradual. This long induction period dates back to the discovery of radioactivity and the development of x-ray tubes. Radium salts, the first radiation sources, were supplanted in the third and fourth decades of this century by x-rays. During this period, pioneering scientists such as Fricke, Lind, Mundt, Risse, and their collaborators laid the foundations of radiation-induced gaseous and aqueous reactions. From these modest beginnings research in this field gradually gathered momentum in the fifth decade by the use of Van de Graaff and cyclotron accelerators and in the sixth through the availability of powerful ^{60}Co γ -ray sources. Finally in the seventh decade the results of basic research exploded into prominence through the use of electron pulse accelerators. In this decade, we are reaping the benefits of these new developments by drawing attention to the applications of radiation chemistry. Since the 1930s the number of active workers in this field has multiplied a hundred-fold, and research has expanded from a few universities and national laboratories to research centers the world over.

The early workers established phenomena connected with the qualitative, and later with the quantitative changes taking place during irradiation. Products and some intermediate species were identified in gases and in aqueous solutions, and work progressed in three areas: dosimetry, radical and ionic yields, and relative rate constants. From these results, speculations regarding the mechanism of energy loss, of free radical and ion pair formation and distribution, were mathematically formulated and tested by the developing specialty of diffusion kinetics.

More recently, assisted by photochemistry, spectroscopy in its varied forms, chromatography, computers, and applied electronics, radiation chemistry is assailing many of the problems associated with the properties of transient species at an unprecedented rate. Commonplace, already, is the study of intermediates lasting only milli- and micro-seconds. A rapidly developing subdivision is on the horizon—that of nanosecond and picosecond chemistry. Knowledge of the nature and rates of these reactions has been of inestimable aid in untangling reaction mechanisms in chemistry and biology. For example, the discovery of the hydrated electron and the determination of its rate constants has aided the interpretation of reactions in aqueous media. Recent studies on solvated and

trapped electrons in liquids and solids assist materially in explaining phenomena in these media. Similarly, the identification of singlet and triplet states in the radiolysis of gases and organic liquids provides data crucial for understanding these complex systems.

The papers reported in these two volumes constitute about two-thirds of those presented at the Argonne National Laboratory-sponsored International Conference on Radiation Chemistry, to which 200 prominent scientists and students from 21 countries and 81 universities and institutes were invited. This conference was in celebration of Argonne National Laboratory's participation in a decade of pulse radiolysis. All phases of radiation chemistry, from the theoretical to the fundamental changes taking place in complex molecules, were included. A special session on dosimetry was planned for Dr. Hugo Fricke on August 15, his 76th birthday, to honor him for his many contributions to radiation chemistry over the past 40 years. The conference papers are assembled in these two volumes: one, largely on aqueous solutions, consists of the survey and original papers given in the aqueous, biological, and dosimetry sessions; the other, largely organic, deals with similar groups of papers on gases, liquids, and solids. The broad scope and interest in these papers reflects the influence and applications of radiation chemistry in most branches of chemistry today.

Argonne, Ill.
July 1968

EDWIN J. HART

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Stabilization of Electrons in Low Temperature Radiolysis of Polar Systems

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This is a review of the results of the authors on the nature and properties of trapped electrons (e^-_{tr}) in irradiated frozen aqueous and alcoholic systems. These species are observed not only in alkaline ices and alcoholic glasses at 77°K. but also in glassy aqueous solutions of NaClO_4 , LiCl , KF , K_2CO_3 , alcohols, HCHO , HCOONa , carbohydrates, etc. In these systems e^-_{tr} has narrow symmetrical singlet at g-factor ~ 2001 in EPR-spectrum and wide optical absorption band in visible region. The yields of e^-_{tr} were measured. In aqueous glasses the e^-_{tr} and $(e^-_{tr})_2$ are mutually transformed under certain conditions. The data obtained by studying the photochemistry of e^-_{tr} indicate the existence of dispersion of trapping energy. The nature of electron stabilization is discussed.

One of the greatest achievements of the radiation chemistry lies in the experimental proof of the electron solvation in various irradiated polar systems (see—e.g., 13, 17, 36) and its stabilization under certain conditions at low temperatures. In the latter case the process may be presented in the form of the following reactions.

The electron knocked out of polar molecule M:



after thermalization



in the absence of the scavengers is captured by trap T:



The process considered is displayed most clearly in the case of glassy polar systems and in the absence of the compounds which are reactive with the electrons.

The present paper sums up the results of the performed investigations of the nature and properties of the trapped electrons in the frozen aqueous and alcohol systems. (The trapped electron marked e^-_{tr} is unmobile which distinguishes it from the solvated electron.)

Experimental Technics

The investigation of the nature and properties of e^-_{tr} involved a wide use of the methods of the electron paramagnetic resonance (EPR) and optical spectroscopy. The EPR spectra were recorded by the RE-1301 radiospectrometer while the optical spectra were registered by the SF-4A spectrophotometer.

During measurements of the EPR spectra, the samples of about 0.05 ml. were irradiated in special ampules made of glass "Luch-2" which did not give any noticeable EPR signal at irradiation (9). The magnetic field was calibrated with the aid of the aqueous solution of Mn^{2+} and benzene solution of α, α' -diphenyl- β -picrylhydrazyl (DPPH). The position of the lines in the spectrum was determined by reference to the position of the lines of solid DPPH. The intensity of the signal was found by double integration with the use of a special nomogram (62). The concentration of the free radicals in the sample was measured by reference to the standards of ultramarine whose content of the paramagnetic particles was determined with the aid of a fresh-prepared solution of DPPH in benzene. A relative error in determination of the radical concentration amounted to $\pm 10\%$. The variation of the radiospectrometer sensitivity in the course of registration was checked by paramagnetic standard $CuCl_2 \cdot 2H_2O$ placed in the resonator of the radiospectrometer. All the EPR spectra were registered under the conditions excluding the microwave power saturation effect.

The photo-annealing of the colored samples by the visible light was effected directly in the resonator of the radiospectrometer during registration of the EPR spectrum. The tungsten lamp, which was provided with the respective light filters, was used as a light source.

The optical spectra were measured with the aid of a special quartz Dewar flask. Its construction practically precluded boiling of the liquid nitrogen in the cell in which the sample was located (48). This prevented accumulation of frozen water and carbon dioxide on the samples. The frozen samples were irradiated in quartz cells of 2–4 mm. in thickness.

The glassy solutions were prepared by a rapid freezing at $77^\circ K$. The transparent samples of the neutral ice were obtained from twice-distilled water subjected to a slow freezing at a temperature of 270° to $272^\circ K$. in special molds. The produced ice plates of about 5 mm. in thickness were irradiated in the sealed ampules at a temperature of $77^\circ K$. After irradiation the ampules were opened and the samples were transferred into the Dewar flask for taking optical measurements.

The experiments involved the use of γ -radiation of ^{60}Co . The dose rate was commonly equal to $\sim 10^{16}$ e.v./ml. sec. The dosimetry was made by the ferrosulfate method. The calculation of the dose was performed while taking into account the difference in electron densities of the dosimetric and investigated solutions.

Water and Aqueous Solutions of Electrolytes

Among the first investigations which showed electron stabilization in the polar "glasses" at low temperatures was the work of Ershov *et al.* (30). This work employed the EPR method to identify e^-_{tr} in the alkaline aqueous solutions irradiated at 77°K. Later on these conclusions were confirmed in a large number of publications (3, 5, 6, 8, 37, 42, 54, 55). (Earlier the optical absorption of e^-_{tr} in the irradiated alkaline glass was detected in other works (see 41, 58).

At the present time it is certain that stabilization of electrons is a general phenomenon. Data have been obtained on the EPR and optical spectra which testify to appearance e^-_{tr} in the neutral or weak alkaline aqueous solutions of such salts as NaClO_4 , LiCl , KF , Na_2HPO_4 , NaH_2PO_4 , carbonates, bicarbonates, formates, etc. (10, 21, 26, 27, 29, 45, 47).

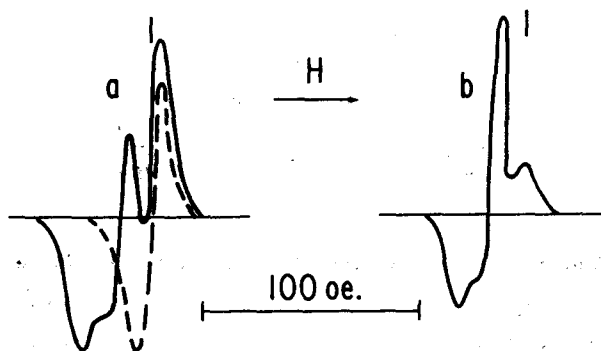


Figure 1. EPR spectrum of glassy 5M K_2CO_3 in H_2O : (a) subjected to γ -irradiation at 77° K. and (b) after illumination with visible light. Dotted line is the EPR spectrum of e^-_{tr} . On Figures 1, 2, 3, 5, 6, 7 and 10 vertical line is the position of the EPR signal of polycrystalline DPPH

The EPR spectrum of e^-_{tr} is essentially a narrow symmetrical singlet with a g -factor of 2.001 ± 0.001 . Figures 1 and 2 show by way of example the EPR spectra of e^-_{tr} in 5M aqueous glasses of K_2CO_3 in H_2O and D_2O (21). From the analysis of the spectra it follows that the width ΔH of the line of e^-_{tr} as measured between the points of maximal slopes

is reduced by two or three times when substituting D_2O for H_2O . Table I gives the ΔH values for a series of systems wherein these values have been measured accurately. The close values of ΔH for e^-_{tr} in the alkaline glasses have been obtained by other authors (6, 8, 37, 54, 55).

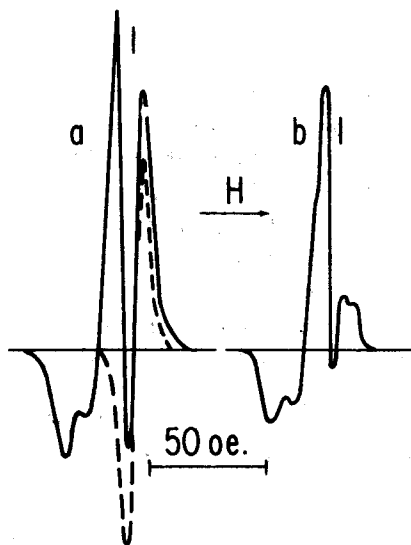


Figure 2. EPR spectrum of glassy 5M K_2CO_3 in D_2O : (a) subjected to γ -irradiation at 77°K. and (b) after illumination with visible light. Dotted line is the EPR spectrum of e^-_{tr}

Table I. Width ΔH of EPR Line of e^-_{tr} in Aqueous Glasses at 77°K.

System	$\Delta H, oe$	References
10M KOH in H_2O	13.4 ± 0.2	19, 30, 32
10M KOD in D_2O	4.6 ± 0.2	19
10M NaOH in H_2O	15.1 ± 0.2	19
10M NaOD in D_2O	6.5 ± 0.2	19
10M $NaClO_4$ in H_2O	14.0 ± 2.0	29
10M $NaClO_4$ in D_2O	5.6 ± 1.0	29
15M LiCl in H_2O	18.0 ± 2.0	29
15M LiCl in D_2O	7.0 ± 1.0	29
5M K_2CO_3 in H_2O	12.0 ± 2.0	21
5M K_2CO_3 in D_2O	5.0 ± 1.0	21

The results given in Table I show that the water molecules are the neighbors of the electron. However, a definite contribution is made also by the interaction of the electron with the alkaline metal ions. From

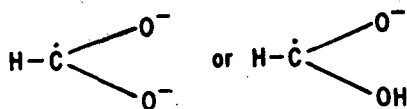
Table I it is seen that ΔH increases in direction from K to Li—i.e., it increases with the growth of the magnetic moments of the alkaline metal nuclei. The e^-_{tr} signal is rapidly saturated with the increase of the microwave power.

The trapped electron is optically absorbed in the visible part of the spectrum. The spectrum is asymmetric, having a more steep drop on the side of long waves. The similar shape of the absorption band is characteristic of the solvated electrons in the polar liquids. Another feature of the spectrum is large half-width $W_{1/2}$ of the band. Table II contains some characteristics of the optical absorption band of e^-_{tr} in the aqueous glasses of electrolytes at 77°K. Analogous optical bands of e^-_{tr} in the alkaline and perchlorate glasses are observed in References 6, 8, 10, 18, 41, and 58.

Table II. Characteristics of Optical Absorption Spectra of e^-_{tr} in Aqueous Matrixes at 77°K.

Matrix	λ_{max} , nm.	$E\lambda_{max}$, e.v.	$W_{1/2}$, e.v.	ϵ at λ_{max} , $M^{-1} cm^{-1}$	References
10M KOH in H ₂ O	585	2.11	0.90	13700 ($\pm 20\%$)	27, 29, 47
10M KOH in D ₂ O	560	2.21	0.87	—	27, 29, 47
10M NaOH in H ₂ O	585	2.11	0.80	—	27, 29, 47
10M NaOH in D ₂ O	560	2.21	0.76	—	27, 29, 47
10M NaClO ₄ in H ₂ O	540	2.29	0.87	—	27, 29, 47
10M NaClO ₄ in D ₂ O	520	2.37	0.80	—	27, 29, 47
5M K ₂ CO ₃ in H ₂ O	535	2.31	0.82	20000 ($\pm 40\%$)	21, 47
5M K ₂ CO ₃ in D ₂ O	510	2.43	0.77	—	21, 47
8M HCOONa in H ₂ O	555	2.23	0.93	12000 ($\pm 40\%$)	45, 47
8M HCOONa in D ₂ O	535	2.31	0.72	—	45, 47

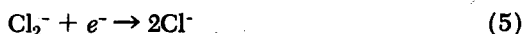
In the presence of the electron scavengers there is observed some drop in the intensities of the EPR signal of the e^-_{tr} and of the respective optical band and a new radical appears which is actually the product of reaction of the electron with the added substance. Thus, the appearance of the ion-radicals of NO₃²⁻ and NO₂²⁻ has been detected in the solutions of nitrate and nitrite (22, 28, 31, 33, 34), O⁻ in the perchlorate glasses (29),



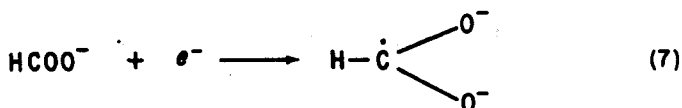
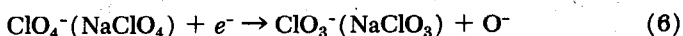
in the formate or formic acid solutions (45, 46, 49), etc. Shown in Figure 3 are the EPR and optical spectra of the NO₃²⁻ ion-radical (22).

The trapped electrons are annealed effectively by the visible light. The rate of annealing increases with the growth of the initial concentra-

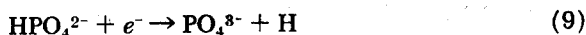
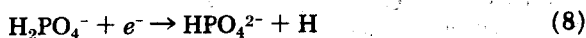
tion of e^-_{tr} and of the other paramagnetic particles. During photo-annealing of e^-_{tr} in the aqueous glasses of the alkalis (30, 32, 47), LiCl (29) and carbonates (21) the concentration of the radicals is generally reduced which is explained by combination of the electrons released from traps with the other radicals. For instance,



In the aqueous glasses of $NaClO_4$ (29) and $HCOONa$ (47) the electrons knocked out by the light quanta partially participate in the reactions with the dissolved substances forming new radicals:



Besides, the concentration of the hydrogen atoms is increased in the aqueous glasses of $NaClO_4$ (29) and acid phosphates (29) as a result of photo-annealing. Thus, the intensity of the doublet signal of H atoms increases by 10 or 20% (in H_2O) and the intensity of the triplet signal of D atoms, by 30 to 40% (in D_2O). Evidently, these results indicate the possibility of additional formation of H atoms in the following reactions in the acid phosphates:



It is quite possible, however, that the additional appearance of the hydrogen atoms in these systems and particularly in the perchlorate glasses is caused by the reactions of the electrons with the ions of H_3O^+ in the spurs.

The yields of e^-_{tr} in the aqueous glasses depends, first, on the nature of the matrix, secondly, on the concentration of the dissolved substance, and thirdly, on the degree of crystallinity of the sample. With increase of the degree of crystallinity of the frozen solution, $G(e^-_{tr})$ becomes less while the rise of the concentration of the electron-inert substance increases the yield.

Most thorough measurements of the e^-_{tr} yields have been taken by the EPR method in the alkaline glasses. In accordance with papers 18, 28, 30, 32, 37, 42, 54, and 55, $G(e^-_{tr})$ for 10M glassy alkaline solution is equal to 1.5–3.0. Such scattering is caused by the errors inherent with the EPR method and by the fact that these yields have been determined at rather considerable absorbed doses when there is no linear relationship between