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RF Project 2035

Report No. COO-1504-2

PROGRESS

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

1314 KINNEAR RD.
COLUMBUS, OHIO 43212

To U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439
Contract No. AT(11-1)-1504

On PULSE RADIOLYSIS OF ORGANIC AND AQUO-ORGANIC
SYSTEMS

For the period February 1, 1966 - May 31, 1967

Submitted by Dr. Leon M. Dorfman
Department of Chemistry

Date July 28, 1967

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PULSE RADIOLYSIS STUDIES OF FAST REACTIONS
IN ORGANIC AND AQUO-ORGANIC SYSTEMS

PROJECT PERSONNEL (for forthcoming contract period.)

L. M. Dorfman	Principal Investigator
P. Neta	Postdoctoral Fellow - from Weizmann Institute of Science
H. Ueda	Postdoctoral Fellow - from Tokyo Institute of Technology
E. G. Wendell	Electronics Technician
J. R. Brandon	Graduate Student - Ph.D. Candidate
R. Casey	Graduate Student - M.Sc. Candidate
B. L. Gall	Graduate Student - Ph.D. Candidate
N. Shank	Graduate Student - Ph.D. Candidate
E. L. Tremba	Graduate Student - M.Sc. Candidate

LINEAR ACCELERATOR

The operation of the Varian V-7715 A linear accelerator in chemistry experiments (as distinct from testing) was begun in late March, 1966, just six weeks after receipt of shipment. With the exception of a single 8-day period for electron gun replacement and a two-week vacation shutdown, the accelerator has continued to operate satisfactorily without any unplanned shutdown in excess of one day.

The electron gun failed on February 21, 1967 after accumulating 1880 hours of gun filament time, well in excess of the specification of 500 hours. With the cooperation of Varian Associates, a new gun was installed and the accelerator put back into operation on March 2, 1967. The cost of the replacement was \$2700.

Machine performance has been excellent. The pulse has rise and decay times of about 6 nanoseconds from 10 to 16 nsec. pulse. Pulse stability has varied from about $\pm 2\%$ to $\pm 5\%$ at most times. There is some problem with what appears to be RF noise pick-up for times less than 1 μ sec. Some progress has been made in eliminating this, and Varian is sending a man in September to advise us.

OPTICAL DETECTION

During this period the detection equipment was used successfully over the range 2,000 Å to 10,000 Å. The best time resolution accomplished so far has been about 40 nanoseconds. Equipment is under construction, and

should be completed in September, 1967, which will permit us to resolve nanosecond and sub-nanosecond times using the accelerator in the stored-energy mode. It is intended to order infra-red detection equipment as the next step to extend the range to about 20,000 Å.

PUBLICATIONS

The following publications have already appeared as a result of the first eight months of operation. Reprints are attached.

Pulse Radiolysis Studies XI: Protonation Reactions of Aromatic Anions in some Aliphatic Alcohols, S. Arai, E.L. Tremba, J.R. Brandon, and Leon M. Dorfman, Canadian J. of Chem., 45, 1119, (1967)

Pulse Radiolysis Studies.X. Electron Transfer Reactions of Aromatic Molecules in Solution, S. Arai, D.A. Grev, and Leon M. Dorfman, J.Chem.Phy., Vol. 46, No. 7, pp.2572-2578, 1 April 1967.

Pulse Radiolysis Studies. IX. Reactions of the Ozonide Ion in Aqueous Solution, W.D. Felix, Bonnie L. Gall, and Leon M. Dorfman, J. Phy. Chem., 71, 384 (1967).

TALKS PRESENTED BY PROJECT PERSONNEL

W. D. Felix - Reactive Species in Oxygenated Water. Gordon Research Conference on Radiation Chemistry, July 1967.

L. M. Dorfman - Electron and Proton Transfer Reactions of Aromatic Molecules in Solution at N. Y. ACS Section, March 1967, Symposium on Photochemistry, University of Minnesota, April 1967, N.Y.U. Chemistry Seminar, May 1967, Gordon Research Conference on Organic Photochemistry, August 1967; Reactive Species in Oxygenated Water, Purdue University, Chemistry Seminar, May 1967.

SUMMARY OF RESULTS

1. Electron Transfer between Aromatic Molecules in Solution.

Absolute rate constants have been obtained, for the first time, for the rate of electron transfer from aromatic radical anions in solution to a second aromatic compound:

Nine donor-acceptor pairs were successfully investigated. Of these, seven had rate constants which appear to be diffusion controlled, but two pairs, significantly exhibited exchange which was considerably slower than diffusion controlled. These two pairs also have the smallest difference in reduction potential. A correlation with the theory of R.A. Marcus (J. Chem. Phys., 43, 679(1965)) is being examined.

2. Protonation of Aromatic Anions in the Aliphatic Alcohols.

Determination of the activation energies as well as absolute rate constants for a series of protonation reactions:

has shown that the pre-exponential factor, rather than the activation energy is the predominant basis for the "low" rate constants. This may be due to an entropy effect related to reorientation of the liquid structure during the transfer. There appeared to be no evidence for quantum mechanical tunnelling.

3. Reactions of the Ozonide Ion in Aqueous Solution.

Continued investigation of the ozonide ion, O_3^- , formed in oxygenated water at $\text{pH} > 12$, has led to the following results. (a) The discrepancies in the literature surrounding the reaction $\text{O}_3^- + \text{O}_3^-$ have been explained as an effect of pulse intensity and oxygen concentration, (b) The inverse oxygen effect suggests an equilibration and/or back reaction, (c) Absolute rate constants have been obtained for the reactions $\text{O}_3^- + \text{HO}_2^-$; $e_{\text{aq}}^- + \text{HO}_2^-$; $\text{O}^- + \text{HO}_2^-$. (d) The rate constant for $\text{O}_3^- + \text{O}_3^-$ is an order of magnitude lower than reported by Boag and Adams. The system is by no means adequately understood.

4. Reactions of OH with Aromatic Compounds in Solution.

The absorption spectrum of the OH-adduct to benzoic acid, $\text{OHC}_6\text{H}_5\text{COOH}$, has been determined with a maximum at $3450 \text{ \AA}$. The results show that the

H-adduct, $\text{HC}_6\text{H}_5\text{COOH}$, absorbs strongly in the same region.

5. Electronic Triplet Energy Transfer between Aromatic Molecules.

The formation rate constant for biphenyl triplet in acetone was found to be lower than that for anthracene and naphthalene. Difficulties of spectral overlap and concurrent kinetics have been encountered in determining transfer rate constants.