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PROGRESS REPORT

FOR CONTRACT NO. EY-76-S-02-1763.*000. [November 1976 through October 1977]

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS

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DISCLAIMER

ERDA CONTRACT NO. EY-76-S-02.1763. *000

PUBLICATIONS FROM INCEPTION OF CONTRACT THROUGH 1977

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J. L. Dye, M. G. DeBacker and L. M. Dorfman, Pulse Radiolysis Studies XVIII. Spectrum of the Solvated Electron in the Systems Ethylenediamine - Water and Ammonia - Water, J. Chem. Phys., 52, 6251 (1970).

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H. Y. Wang, J. A. Eyre and L. M. Dorfman, Activation Energy for the Gas Phase Reaction of Hydrogen Atoms with Carbon Monoxide, J. Chem. Phys., 59, 5199 (1973).

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J. R. Clement, N. T. Lee, M. H. Klapper and L. M. Dorfman, Pulse Radiolytic Investigation of Single Heme Group Reduction in Human Methemoglobin, J. Biol. Chem., 251, 2077 (1976).

R. J. Sujdak, R. L. Jones and L. M. Dorfman, Rate Constants for Some Electrophilic Reactions of Benzyl, Benzhydryl and Trityl Cations in Solution, J. Amer. Chem. Soc., 98, 4875 (1976).

L. M. Dorfman, R. J. Sujdak and B. Bockrath, Fast Reaction Studies of Carbanions and Carbocations in Solution, Accounts Chem. Res., 9, 352, (1976).

L. M. Dorfman, Y. Wang, H. S. Wang and R. J. Sujdak, The Formation of Carbonium Ions, Carbanions and Carbanion Pairs in Irradiated Solutions and the Absolute Reactivity of These Intermediates, Faraday Society Discussion, No. 63, 149 (1977).

K. Ho, M. H. Klapper and L. M. Dorfman, Kinetics of Carbon Monoxide Binding to Singly Reduced Human Methemoglobin, J. Biol. Chem., 252, 000 (1977) (In press - December).

TALKS PRESENTED BY PROJECT PERSONNEL

The following talks were given on topics relating to project research:

L. M. Dorfman

Faraday Discussion No. 63 on Radiation Effects in Liquids and Solids, Leicester, England, March 1977, "The Formation of Carbonium Ions, Carbanions and Carbanion-Pairs in Irradiated Solutions, and the Reactivity of These Intermediates".

Radiation Research Society, 25th Anniversary Meeting, San Juan, Puerto Pico, May 1977. Refresher course lecture, "Applications of Pulse Radiolysis".

Société de Chimie Physique, Symposium on Protons and Ions Involved in Fast Dynamic Phenomena, Paris, France, November, 1977, "Fast Reaction Studies of Carbanions and Carbocations in Solution". (Plenary Lecture).

M. Faraggi

American Chemical Society Meeting, Chicago, Ill., August, 1977. "Fast Kinetic Studies of One-Electron Transfer Processes in Proteins".

SUMMARY OF RESULTS

This summary contains results of research of the past year, in two areas for which the results cited are either already in publication, or at the publication stage, or being prepared for publication. Reprints and preprints are attached. The two areas and their content are:

I. Formation, Properties and Reactivity of Molecular Ionic Species in Irradiated Liquid Systems.

(a) Formation Constants for Carbocations and for Cation Radicals in Dichloroethane.

(b) Reactivity of Benzyl Cation and Benzhydryl Cation with Water in DCE.

II. Pulse Radiolysis of Elementary Reactions in Protein Function.

(a) Kinetics of Carbon Monoxide Binding to Singly Reduced Methemoglobin.

(b) One-Electron Transfer in Proteins; Formation of a Histidyl Radical Species.

The results obtained are briefly the following.

I, (a) Formation constants of arylcarbenium ions and of cation radicals in 1,2-dichloroethane have been obtained for a variety of precursor compounds. The reaction under observation is presumably a charge transfer from the precursor compound to a solvent cation or cation radical.

$$RCl\cdot^{+} + Ph_2CBr = Ph_2C^{+} + Br\cdot + RCl$$

The values of the rate constants are of interest in the context of understanding the nature of the hole transport process in irradiated liquids. The specific question is whether such hole transport is purely a diffusive process (hence $k \leq k_{diff}$), or whether some ultra-fast process, which has variously been referred to as a "resonant charge transfer process" occurs. (See paper by Dorfman, Wang, Wang and Sujdak in Disc. Faraday Soc., No. 63, 1977 and discussion by A. Hummel, Interuniversity Research Reactor, Delft). The rate constants we obtain in DCE for a variety of precursor compounds, shown in the

Table, range from 4×10^7 $M^{-1}sec^{-1}$ to 1.6×10^{10} $M^{-1}sec^{-1}$ at 24°C. Since an estimate, from the Smoluchowski equation, gives the value of the diffusion limited rate constant as 0.9×10^{10} $M^{-1}sec^{-1}$, we cannot conclude, in view of

Formation Constants of Cations and of

Cation Radicals in 1,2-DCE at 24°C

Cation Formed	Precursor Compound	Formation Constant ($M^{-1}sec^{-1}$)
$PhCH_2^+$	$(PhCH_2)_2Hg$	1.3×10^{10}
Ph_2CH^+	Ph_2CHBr	1.6×10^{10}
Ph_2CH^+	Ph_2CHOH	4×10^{7}
Ph_3C^+	Ph_3CBr	8.4×10^{9}
Ph_3C^+	Ph_3COH	5.7×10^{8}
Ph_3C^+	Ph_3CCl	4.0×10^{8}
$Ph_2{\cdot}^+$	Ph_2	1.4×10^{10}
$p\text{-}Ph_3{\cdot}^+$	$p\text{-}Ph_3$	1.45×10^{10}

the uncertainty in this estimate, that even the highest values (which exceed k_{diff} by less than a factor of two) in the Table, represent anything but a diffusion limited value. The formation curve for p-terphenyl cation radical, observed at 960 nm, a band selected because it is completely outside the solvent transient absorption region, shows no fast formation process during the pulse.

I. (b) Among the various electrophilic reactions of the aromatic substituted carbocations which we have investigated, is the reaction of the carbocation with water in DCE, for both benzyl cation and benzhydryl cation.

$$PhCH_2^+ + HOH \xrightarrow{k_m} PhCH_2\overset{+}{O}H \rightarrow PhCH_2OH + H^+ .$$

This type of reaction, known in organic chemistry, is a condensation with the nucleophile, followed by a deprotonation. Since the carbocation is formed radiolytically in our system, the foregoing reaction should ensue. It does,

and exhibits an interesting characteristic. The pseudo-first order rate constants obtained for the decay of the cation, when plotted against concentration of water (10^{-2} to 6×10^{-2} M) are non-linear, showing an increase in slope with increasing concentration of water. The data may be linearized by invoking a similar reaction with water dimer:

$$PhCH_2^+ + (H_2O)_2 \xrightarrow{k_d} PhCH_2\overset{+}{O}HOH_2 \rightarrow PhCH_2OH + H_3O^+ \quad .$$

with the appropriate equilibrium involved:

$$2H_2O \underset{}{\overset{K_e}{\rightleftharpoons}} (H_2O)_2$$

and with $k_d > k_m$. The differential rate equation is:

$$\frac{-d[PhCH_2^+]}{dt} = (k_m[H_2O] + k_dK_e[H_2O]^2)[PhCH_2^+] \quad .$$

The linearization gives values of k_m amd k_dK_e. Since K_e is known (0.54 at 24°C) from activity coefficient data for the DCE-H_2O system, k_d can be obtained. Our results for benzyl cation and benzhydryl cation in DCE are:

Rate Constants for Reaction of Carbocations
with Water Monomer and Dimer in DCE. ($M^{-1}sec^{-1}$)

Cation	k_m	k_d
$PhCH_2^+$	1.8×10^7	6×10^8
Ph_2CH^+	1.3×10^6	1×10^8

The reaction exhibits a negative temperature coefficient which, for k_dK_e can be attributed to decrease in K_e with increasing temperature. k_m shows a negative activation energy of -2 ± 1 kcal/mole.

Reaction with the dimer produces a hydrogen bonded stabilized species from

which the proton is detached in the form H_3O^+. This is likely responsible for the higher value of k_d.

II. (a). Our pulse radiolytic investigation of the kinetics of carbon monoxide binding to single-reduced methemoglobin:

$$Hb(Fe^{III})_3Fe^{II} + CO = Hb(Fe^{III})_3Fe^{II}CO$$

has been completed, and a paper is in press. The rate constant for this reaction, at a methemoglobin concentration of 2×10^{-5} M, is found to be 4.1×10^6 $M^{-1}sec^{-1}$ as observed by both decay of the reactant species and formation of the product species. When inositol hexaphosphate is added to the solution, which shifts the dimer-tetramer equilibrium in hemoglobin to the tetrameric state, the rate constant for CO-binding is reduced to 1.1×10^5 $M^{-1}sec^{-1}$. Our observations are consistent with currently held models which explain the biphasic kinetics in terms of the dimer and tetramer in the R-state as the more reactive species, and the tetramer in the T-state ($k = 1.1 \times 10^5$) as the less reactive species. The values for these rate constants also compare closely with data obtained by other methods for the Fe^{III}-Fe^{II} valency hybrids.

II. (b). Our pulse radiolysis studies of the one-electron reduction of five proteins has led to some new information about the nature of the optical band at 360 nm which is formed. Whereas the well-known band at 410 nm is associated with a disulfide radical anion, we conclude from our observations that the 360 nm band is associated with an electron-adduct of an imidazole group. The titration curves obtained for the histidyl radical in trypsin and α-chymotrypsin are consistent with a $pK_a < 4.5$ for the active site histidines of these two proteins. From consideration of the rate constants for attachment of e^-_{aq} to the various residues, the relative population of these groups in the protein,

and their accessibility in the protein structure (for α-chymotrypsin only) we suggest that the carbonyl groups are the predominant site of electron attachment, and that the 410 nm and 360 nm species are formed by internal electron migration in structural elements of the protein.

CURRENT PUBLICATIONS

Papers Published (November 1976 through October 1977)

L. M. Dorfman, Y. Wang, H. S. Wang and R. J. Sujdak, The Formation of Carbonium Ions, Carbanions and Carbanion Pairs in Irradiated Solutions and the Absolute Reactivity of These Intermediates, Faraday Society Discussion, No. 63, 149 (1977).

K. Ho, M. H. Klapper and L. M. Dorfman, Kinetics of Carbon Monoxide Binding to Singly Reduced Human Methemoglobin. J. Biol. Chem., 252, 000 (1977)(In press - December).

Papers Submitted

M. Faraggi, M. H. Klapper and L. M. Dorfman, Fast Reaction Kinetics of One-Electron Transfer in Proteins: The Histidyl Radical; Mode of Electron Migration. (Submitted to J. Phys. Chem.)

Papers in Preparation

Y. Wang and L. M. Dorfman, Reactivity of Benzyl Cation and of Benzhydryl Cation with Water in Solution.

L. M. Dorfman, V. DePalma and Y. Wang, Fast Reactions of Carbocations in Solution, Proceedings of Symposium of 30th International Meeting of Societé de Chimie Physique, Paris, November, 1977.

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