

PROGRESS REPORT

FOR CONTRACT NO. AT(11-1)-1763 [November 1974 to October 1975]

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

PULSE RADIOLYSIS STUDIES OF FAST  
REACTIONS IN MOLECULAR SYSTEMS

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PUBLICATIONS (Immediate past contract  
period to October, 1975)

Papers Published. (November 1974 to October 1975)

J. F. Gavlas, F. Y. Jou and L. M. Dorfman, Optical Absorption Spectrum of the Solvated Electron in Some Liquid Amides and Amines, J. Phys. Chem., 78, 2631 (1974). *removed*

B. Bockrath and L. M. Dorfman, Protonation Rate Constants and Optical Absorption Spectra of Benzyl Carbanion Pairs in Tetrahydrofuran Solution, J. Amer. Chem. Soc., 97, 3307 (1975). *removed*

J. F. Gavlas and L. M. Dorfman, Structure in the Optical Absorption Spectrum of the Solvated Electron?, Int. J. Rad. Phys. and Chem., 7, 227 (1975). *removed*

B. Bockrath and L. M. Dorfman, Ionic Aggregation of the Solvated Electron with Lithium Cation in Tetrahydrofuran Solution, J. Phys. Chem., 79, 1509 (1975). *removed*

Papers in Press.

L. M. Dorfman and J. F. Gavlas, Optical Absorption Spectrum of the Solvated Electron in Polar Liquids and in Binary Solutions, Proceedings of the 5th International Congress of Radiation Research (Seattle 1974), Academic Press (in press).

Papers in Preparation.

J. R. Clement, N. T. Lee, M. H. Klapper and L. M. Dorfman, Pulse Radiolytic Investigation of Single Heme Group Reduction in Human Methemoglobin.

R. Sujdak, R. L. Jones and L. M. Dorfman, Kinetics of Reactive Aryl Carbonium Ions in Solution.

TALKS PRESENTED BY PROJECT PERSONNEL

The following talks were given on topics resulting from project research.

L. M. Dorfman

Colloque Weyl IV, Electrons in Fluids, East Lansing, Mich., July, 1975, 'Ionic Aggregation of the Solvated Electron with Alkali Metal Cations: Lithium in Tetrahydrofuran.'

Hart International Conference on Radiation Chemistry, Argonne, Ill., July, 1975, 'Pulse Radiolytic Investigation of Single Heme Group Reduction of Human Aquomethemoglobin.'

B. Bockrath

Colloque Weyl IV, Electrons in Fluids, East Lansing, Mich., July, 1975, 'The Solvated Electron as Reducing Species in the Formation of Reactive Carbanions.'

SUMMARY OF RESULTS

This summary of results consists only of those research items (a. reactivity of aryl carbonium ions, b. single heme group reduction in human methemoglobin) which are in a reasonably advanced state of progress, but which are not yet sufficiently complete as to have been submitted for publication. Those research topics on which publications have appeared during the past contract year (a. the solvated electron, b. reactivity of aryl carbanions) are not reviewed in this summary since details are available in the accompanying reprints. Four such reprints are enclosed; one paper is in press and two more are in preparation. The following is a summary of the highlights of the work on carbonium ions and on methemoglobin.

#### I. Reactivity of Aryl Carbonium Ions in Solution.

Having generated and observed the benzyl cation,  $C_6H_5CH_2^+$  [Jones and Dorfman, J. Am. Chem. Soc., 96, 5715 (1974)] in dichloroethane by pulse radiolysis with various benzyl compounds, we have gone on to study the reactivity of benzhydryl cation  $(C_6H_5)_2CH^+$ , and of trityl cation,  $(C_6H_5)_3C^+$ , as well. Absolute rate constants for electrophilic reactions of these carbonium ions with various aliphatic amines and with aliphatic alcohols, have been determined. Although not all the systematic kinetic constants for these various nucleophiles we are studying have been determined, the following results for the reactivity of benzyl cation and of benzhydryl cation with triethylamine, tripropylamine and tributylamine are of interest.

Rate Constants for the Reaction of Aryl  
Carbonium Ions with Amines in Dichloroethane at 25°C.

(Constant is given in units of M<sup>-1</sup>sec<sup>-1</sup>)

	Benzyl Cation	Benzhydryl Cation
triethylamine	2.0 x 10 <sup>9</sup>	1.2 x 10 <sup>9</sup>
tri-n-propylamine	1.4 x 10 <sup>9</sup>	7.7 x 10 <sup>8</sup>
tri-n-butylamine	1.0 x 10 <sup>9</sup>	5.3 x 10 <sup>8</sup>

The reactivity ratio for benzyl/benzhydryl appears to be 1.8. Effects in the amine series are likely steric effects. Determination of trityl cation reactivity is in progress.

Reactivity of the foregoing aryl carbonium ions with methanol, ethanol and 2-propanol is considerably lower with the alcohol monomer, the rate constants falling in the range 2 x 10<sup>7</sup> to 9 x 10<sup>7</sup>. The kinetics are complex, indicating a higher reactivity with alcohol dimer in solution than with monomer.

The reactivity of the aryl carbonium ions with bromide and iodide ion in DCE is considerably higher with rate constants of approximately 5 x 10<sup>10</sup>, very likely the diffusion-controlled limit. A manuscript is in the initial stage of preparation.

II. Single Heme Reduction in Human Methemoglobin. (Jointly with Professor M. Klapper)

Reduction of the iron in human aquomethemoglobin A has been investigated by the pulse radiolysis method under concentration conditions such that only a single heme group is reduced. The reactivity of the hydrated electron with methemoglobin was determined by direct observation of this species. The separate reactions of OH-radical and of H-atom, as well

as of  $e_{aq}^-$ , were studied by observing absorption changes in the hemoglobin over the wavelength range 290 to 600 nm, with appropriate scavengers ( $N_2O$ ,  $CH_3OH$ ) in solution.

In unbuffered aqueous solutions at pH 6.2, in 0.1 M NaCl solution at 23°C, the rate constants for the disappearance of  $e_{aq}^-$ , and for the reduction of heme iron as measured by the absorbance increase at 435 nm, were found to be the same, namely  $4.2 \times 10^{10} M^{-1}sec^{-1}$ . It was also found that 55% of the hydrated electrons formed were effective in reducing the heme iron. This equivalence of rate constants together with the incomplete material balance in  $e_{aq}^-$  can be understood simply in terms of concurrent competing reactions of  $e_{aq}^-$  by more than one pathway; it does not call for a model involving a rate-determining activated complex in the reduction mechanism, as proposed by Wilting, et al. The rate constants for the reaction of  $e_{aq}^-$  with cyanomethemoglobin, with azidomethemoglobin and with deoxyhemoglobin are being determined.

The hydroxyl radical does not contribute to the fast heme-reduction process, which is produced by the hydrated electron. On a time scale of 100  $\mu$ secs and longer, however, spectral observations in  $N_2O$ -saturated solutions reveal that about one-tenth of the hydroxyl radicals (a strong oxidizing species) results in reduction of the heme group. This suggests that OH produces a radical intermediate in the methemoglobin, capable of reducing the heme iron of the protein. A manuscript is in the final stages of preparation.



Publications (during period November 1974 to October 1975)

J. F. Gavlas, F. Y. Jou and L. M. Dorfman, Optical Absorption Spectrum of the Solvated Electron in Some Liquid Amides and Amines, J. Phys. Chem., 78, 2631 (1974).

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