RF Project 2589

Report No. COO-AT1763-16

MASTER

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

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To   U.S. Atomic Energy Commission

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Argonne, Illinois 60439

On   Pulse Radiolysis Studies of Fast

Reactions in Molecular Systems

For the period 19 August 1969 to 27 August 1970

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Date August 27, 1970

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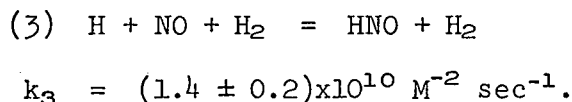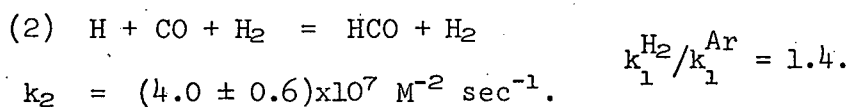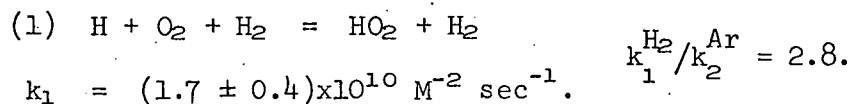
SUMMARY OF RESULTS

I. Reaction Kinetics of Gaseous Hydrogen Atoms by Fast Lyman-α
   Absorption Spectrophotometry.

The pulse radiolysis method has been used to produce ground-state
hydrogen atoms in gaseous hydrogen, and has been combined with fast
Lyman-α (1215.7A°) absorption spectrophotometry to observe these atoms
directly with microsecond time resolution in kinetic studies. This
resonance absorption technique has now been used to investigate several
bimolecular addition reactions of gaseous hydrogen atoms.

We have also carried out a direct test of the validity of applying
Beer's Law with the Lyman-α line in our system by using repetitive pulses
of electrons to build up integral multiples of the initial hydrogen atom
concentration in hydrogen. The results show that the deviation from
Beer's Law over the range of optical density used in our experiments is
so small as to require no correction to the observed optical absorption.

The absolute rate constants, at 25°C, for the addition reaction of
H-atoms with O_2, CO and NO, and the relative third-body efficiencies of
hydrogen and argon in these reactions, are:

$$(1) \quad H + O_2 + H_2 \;=\; HO_2 + H_2 \qquad k_1^{H_2}/k_2^{Ar} = 2.8.$$

$$k_1 \;=\; (1.7 \pm 0.4)\times10^{10} \; M^{-2} \; sec^{-1}.$$

$$(2) \quad H + CO + H_2 \;=\; HCO + H_2 \qquad k_1^{H_2}/k_1^{Ar} = 1.4.$$

$$k_2 \;=\; (4.0 \pm 0.6)\times10^{7} \; M^{-2} \; sec^{-1}.$$

$$(3) \quad H + NO + H_2 \;=\; HNO + H_2$$

$$k_3 \;=\; (1.4 \pm 0.2)\times10^{10} \; M^{-2} \; sec^{-1}.$$

The question concerning the specific rate of H-atom addition to
ethylene has been resolved by our determination of the high-pressure
limiting rate constant at pressures sufficiently high for rapid collision-
al de-excitation of vibrationally excited ethyl radical. The value, at
25°C, is:

$$(4) \quad H + C_2H_4 \;=\; C_2H_5^{*}$$

$$k_4 \;=\; (5.5 \pm 0.5)\times10^{8} \; M^{-1} \; sec^{-1}.$$
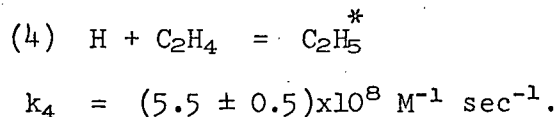
In this determination, we have taken advantage of the fact that it is quite
feasible, with our method, to work at high pressure, and k_4 has been de-
termined at 800 to 1800 torr hydrogen. Previous determinations at low

pressure, which involved also the decomposition of $C_2H_5{}^*$, had required an extrapolation to high pressures to arrive at a value for k_4.

II. Kinetics of Aromatic Radical Ions in Solution.

(1) Solvent Effects in Electron Transfer Reactions of Aromatic Radical Anions.

According to the theory of R. Marcus for the specific rate of electron transfer reactions in solution, the two major factors which determine the free energy of activation for such reactions are: (a) the standard free energy of the reaction, and (b) the solvent reorganization energy, resulting from the reorganization of the solvation shell from around the donor anion to include the acceptor in the transition state as the acceptor anion is formed.

In studying the electron transfer of aromatic radical anions in alcohol solvents:

$$A_1^- + A_2 = A_1 + A_2^- \tag{5}$$

we had already reported data which show that the contribution of the standard free energy is adequately described by the theory. We have now determined k_5 for the transfer from pyrenide ion to 9,10-dimethylanthracene in four different solvents: ethanol, 2-propanol, ethylenediamine and diethylamine. These solvents represent a series of liquids in which the solvent reorganization energy of Marcus theory [which is a function of the dielectric properties of the solvent, that is of $(1/D_{op} - 1/D_s)$] varies from 8 to 17 kcal./mole. Over this limited range, the data show that the contribution of the solvent reorganization energy to the free energy for activation of the electron transfer reaction, on a relative basis, is adequately described by the theory. The details have been presented in two of the publications, Brandon and Dorfman, J. Chem. Phys., 53, Oct. 15 (1970), and Dorfman, Accounts Chem. Res., 3, 224 (1970).

(2) Solvent Effects in Proton Transfer Reactions of Aromatic Radical Anions.

The effect of solvent on the rate of protonation of an aromatic radical anion by an alcohol:

$$A^- + ROH = AH^* + RO^- \tag{6}$$

using the reaction of diphenylide ion as a representative system to probe these solvents effects:

$$C_{12}H_{10}^- {}^* + ROH = C_{12}H_{11}{}^* + RO^- \tag{7}$$
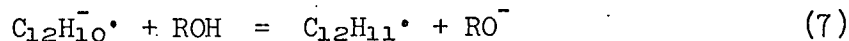
has now been studied in a number of mixed solvent systems, namely: ethanol-ethylenediamine, ethanol-cyclohexane, ethanol-triethylamine, ethanol-diethylamine, ethylene glycol-ethylenediamine and ethylene glycol-

triethylamine. In the alcohol-amine systems the first order rate constant for the protonation reaction was drastically <u>reduced</u> in amine-rich solution over a broad concentration range and <u>increased</u> in alcohol-rich solution over a narrow concentration range. The rate constant was <u>increased</u> at all concentrations in the ethanol-cyclohexane system. These are profound effects, the magnitude of the rate constant ranging over more than three orders of magnitude relative to the value in the pure alcohol.

The reduction of the rate constant for the anion decay by the amine solvent is attributed to the formation of a hydrogen-bonded complex between the amine and the alcohol which reduces the lability of the available hydrogen. The increase of the rate constant by addition of cyclohexane is attributed to the solvent structure-breaking effect of the cyclohexane in the polar protic alcohol. The increase by the addition of a small amount of amine to the alcohol is not at all understood at present. The details of these preliminary results have been presented in the paper by Brandon and Dorfman.

III. The Solvated Electron in Weakly Polar Liquids and in Mixed Solvent Systems.

(1) Weakly Polar Liquids.

With the satisfactory performance of our fast infra-red detection system it has now been possible to determine the optical absorption band of the solvated electron in weakly polar liquids, such as tetrahydrofuran, out to wavelengths beyond 20,000 A^o in the liquid solvent at room temperature. The binding of the electron in THF, as expected on the basis of the dielectric properties, is considerably weaker than in strongly polar liquids such as water, ammonia and the aliphatic alcohols. The absorption maximum in THF is at $2 \cdot 1 \pm 0 \cdot 1$ u, considerably farther into the infra-red than had been suggested in earlier photochemical work.

(2) Mixed Solvents.

The optical absorption band of the solvated electron has been determined in the following mixed solvent systems: ammonia-water, ethylenediamine-water, tetrahydrofuran-water, tetra-hydrofuran-ethylenediamine. The dependence of λ-max and of the band half-width upon composition in the ammonia-water and ethylenediamine-water systems indicates that in these mixed solvents the electron is sampling the aggregate properties of the solution. Details have been presented in the paper by Dye, DeBacker and Dorfman, J.Chem.Phys., <u>52</u>, 6251 (1970). This appears to be true also, perhaps to a somewhat lesser extent for tetrahydrofuran-ethylenediamine. In the tetrahydrofuran-water system, on the other hand (a weakly polar and a strongly polar liquid) the electron seems to be sampling the water predominantly, judging from the small gradual shift in λ-max as THF is added.