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**ESR STUDIES OF ELECTRON TRANSFER IN TRI-p-TOLYLAMINE,
PHENOTHIAZINE AND DIBENZO-p-DIOXIN RADICAL CATION SYSTEMS**

by

Soren P. Sorensen

A DISSERTATION

**Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy
Department of Chemistry**

Under the Supervision of Professor Walter H. Bruning

Lincoln, Nebraska

July, 1972

TITLE

ESR STUDIES OF ELECTRON TRANSFER IN TRI-p-TOLYLAMINE, PHENOTHIAZINE
AND DIBENZO-p-DIOXIN CATION SYSTEMS

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TO MY WIFE

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I. INTRODUCTION

Electron spin resonance (ESR) has been used extensively in recent years to study rates and mechanisms of rapid electron transfer processes between neutral parent molecules and free-radicals derived from them. The majority of this work has been devoted to the study of aromatic anion systems; whereas, comparatively little work of this sort has been performed on cation systems. This work concerns rate studies on various organic cation systems and how these rates are effected by solvent and dissolved salts.

1.1 ESR SPECTROSCOPY

All forms of spectroscopy are based on the observation of transitions between the various energy levels of molecules, atoms or nuclei. The spectroscopic variation of major interest in this work concerns molecules which possess an unpaired electron, i.e., free radicals. When such species are placed in a strong magnetic field \vec{H}_0 , an interaction results between the magnetic moment of the electron and \vec{H}_0 . This interaction gives rise to the well known quantized Zeeman energy levels for the electron in a field. The system of spins will distribute themselves between the allowable energy levels in such a way that a small excess will be in the lower energy state (this excess depends on both the magnitude of \vec{H}_0 and the absolute

temperature T). Irradiation with a time dependent magnetic field of the proper frequency $\vec{\omega}_0(t)$ and orientation will induce transitions between the energy levels with energy being absorbed by the spin system from the irradiating field. $\vec{\omega}_0(t)$ and \vec{H}_0 are related by the Larmor precession theorem, i.e., $\vec{\omega}_0 = \gamma \vec{H}_0$, where γ is a constant depending on the mass, charge and g-factor of the electron (obvious analogies exist for nuclei). The energies associated with these transitions, in a static field of 3 kilogauss, are in the frequency range of 9 kilomegacycles.

Generally in any molecule there are nuclei which have magnetic moments that can interact with the magnetic moment of the electron, splitting the electron Zeeman levels into sublevels. This gives rise to hyperfine splitting of the primary Zeeman levels because of the magnetic interaction between the electron spins and the nuclear spins via the Fermi contact interaction. Further aspects of this theory and the wealth of experimental results and applications are described in several sources,^{1,2,3,4,5} and will not be dwelled upon here.

2.) ELECTRON TRANSFER KINETICS via ESR TECHNIQUES

The use of esr spectroscopy to solve chemical problems has grown popular in recent years. Its use as an analytical tool to study electron transfer processes is of prime importance. The significance of this technique lies in its

ability to provide information about very fast reactions (processes which lie in the range of 10^5 to 10^{12} sec $^{-1}$) from measurements on paramagnetic systems that are chemically at equilibrium.⁶

The studies discussed in this thesis concern electron exchange between a neutral precursor and its cation in various chloroform-acetonitrile mixtures. A generalized expression can be written:



Assuming a bimolecular reaction the electron transfer rate can be written:

$$\text{Rate} = \frac{[N]}{\tau_N} = \frac{[N^+]}{\tau_{N^+}} = k[N][N^+] \quad (2)$$

where $[N]$ is the concentration of neutral material, $[N^+]$ is the concentration of free radical, τ_{N^+} is the mean lifetime between exchanges for a paramagnetic cation, τ_N is the corresponding lifetime of the diamagnetic material.

For esr experiments

$$\frac{1}{\tau_{N^+}} = k[N]. \quad (3)$$

Equation (3) shows the need to obtain the mean lifetime between exchanges for paramagnetic cations and also the

molar concentration of the neutral material in the exchanging system in order to calculate the desired second order rate constant k . The molar concentration of the neutral material can be obtained directly. T_N^* is related to the esr experimental linewidth since a decrease in T_N^* relates to an uncertainty in the energy levels of the paramagnetic cation and thus resulting in a broadening of the esr line. This topic has been discussed in the literature in detail.^{6,7}

Theoretical treatment of this problem has been reported by several authors.^{8,9,10,11} Most treatments made use of the Bloch equations¹² to explain a number of reaction-rate lineshape problems.

Piette and Anderson¹³ extended earlier methods to N site exchanges and derived an expression for the total transverse magnetization of spins in environment j .

$$M_T = \frac{-\omega_1 M_0 \sum_j P_j \left[\frac{1}{T_1'} + i \Delta \omega_j \right]^{-1}}{\sum_j P_j \left[\left(\frac{1}{T_2} \right)_j + i \Delta \omega_j \right] \left[\frac{1}{T_1'} + i \Delta \omega_j \right]^{-1}} \quad (4)$$

where M_0 is the equilibrium magnetization, $\omega_1 = \gamma H_1$, γ is the gyromagnetic ratio, H_1 is the alternating magnetic field, P_j is the fraction of spins in environment j , T_2 and T_1' are relaxation times, $\Delta \omega_j$ is the frequency difference between two sites. Since equation (4) contains a summation in both the numerator and denominator, it is apparent that an analytical solution would be difficult even

in the simplest case. Much difficulty would also be encountered in trying to isolate the imaginary part of this expression. This is necessary since the lineshape is given by the imaginary or out-of-phase component.

In certain limiting cases it is possible to derive simple forms of this line shape equation which apply to the limit of slow and fast exchange rates. The equations for these two limiting cases are as follows.

A. FAST EXCHANGE APPROXIMATION

In this limit electron exchange is so rapid that all the hyperfine lines are coalesced into one sharp resonance line. This occurs because the uncertainty in the hyperfine energy levels, in frequency terms, becomes greater than their separation and the electron sees only an average over the energy levels. In other words, the resolution of hyperfine levels is impossible due to a chemical exchange-induced rapid relaxation.

By applying the appropriate assumptions and approximations to equation (4), the expression for the second order rate constant k in this exchange region is obtained¹³

$$k = \frac{2.04 \times 10^7 \nabla}{[N] \Delta H} \quad (5)$$

∇ is the second moment of the hyperfine spectrum in the

absence of exchange, $[N]$ is the molar concentration of the neutral material, ΔH is the linewidth as measured from the points of extreme slope on the first derivative curve. A discussion of spectral moments is given in references (5) and (14).

The slope of the plot of ΔH versus $1/[N]$ can be related to k . This approach has been used by numerous authors¹⁵⁻²¹ to obtain the second order rate constant for electron exchange in various systems in the region of fast exchange.

B. SLOW EXCHANGE APPROXIMATION

In this limit the rate of electron exchange is such that a broadening of each of the esr hyperfine lines results. By applying the appropriate assumptions and approximations to equation (4) the expression for the second order rate constant in this exchange region is obtained¹³

$$k = \frac{1.52 \times 10^7 \Delta H}{(1 - P_j) [N]} \quad (6)$$

ΔH is the contribution to the linewidth due to exchange as measured from the points of extreme slope on the derivative curve, $1 - P_j$ is a correction factor which takes into account the degeneracy of the various nuclear states in a multiple line spectrum.

The slope of a plot of ΔH versus $[N]$ can be related to k . This approach has also been widely used²²⁻³² to obtain the second order rate constant for electron exchange in various free radical systems.

3.) THEORETICAL RESTRICTIONS ON THE SIMPLE FAST EXCHANGE EXPRESSION

Johnson and Holz³³ have made an analysis of the theoretical restrictions on obtaining rate constants using equation (5). Among the criteria which they stated for equation (5) to be valid were:

- A. ΔH versus $1/[N]$ should be a linear plot.
- B. The intercept of ΔH versus $1/[N]$ should yield a reasonable value of the natural linewidth of the hyperfine lines in the absence of exchange.
- C. Lorentzian lineshape of the collapsed spectral line is required.

As will be shown later, criteria (A) and (C) have been met by the systems studied in this work, but admittedly, experimental errors in this type of work are great enough to mask any slight nonlinearity and any small deviation from Lorentzian lineshape. Criterion (B) is not a very sensitive test due to the large uncertainty in the intercepts obtained in many systems.

A more stringent criterion for the use of equation (5) was developed by Johnson and Holz,³³ and depends on the

quantity given by equation (7)

$$Z = \frac{\sqrt{3}}{2} \left(\frac{\Delta H}{\sqrt{V}} \right). \quad (7)$$

Z is an experimentally obtained quantity where ΔH is the linewidth and V in the second moment. It is a guide to determining whether the data used are within the region of approximations necessary for use of equation (5). They found that the experimental data points of the ΔH versus $1/[N]$ plot must have Z values less than 0.2 in order that the rate constant calculated using equation (5) will fall within a 5% limit of error.

In the same paper³³ a method was described which involves corrections utilizing the fourth moment¹⁴ of the uncollapsed hyperfine spectrum, thus allowing one to correct results to the 5% error limit even though Z values were in the range of 0.4.

4. STATEMENT OF THE PROBLEM

Considerable attention has been directed toward rate studies in anion systems using the region of slow or fast exchange.¹⁵⁻³⁰ By use of computer simulation techniques Malinoski, et al.,²¹ were able to use the intermediate region of exchange to obtain information about the electron transfer process. In these studies considerable work was directed toward determining how such factors as solvents,

cations, structural groups, or conformation effect the rate process.

Only limited electron transfer studies have been published using cation systems, all of these being in the region of slow exchange.^{31,32} It has recently been brought to our attention that Bard, et al.,³⁴ have completed a study on some radical ion-neutral parent exchanging systems using the fast exchange limit, which included rate studies on some cation systems in acetonitrile. Included in this is a study on the phenothiazine system and a comparison to our results will be discussed later.

Due to the obvious lack of kinetic data reported for electron exchange between cation radicals and their neutral parent molecules in various solvent mixtures, it was believed important to collect data on such systems.

Tetramethylbenzidine was first considered for rate studies using the fast exchange limit. It was our intent to study electron exchange in this system which contains neutral tetramethylbenzidine, the monocation, and the dication. Both the monocation and the dication can be produced by oxidation with iodine.³⁵ The complications encountered upon analysis of this system led us to consider simpler systems.

Tri-p-tolylamine (TPTA) and phenothiazine (PTAZ) were studied in various chloroform-acetonitrile solvent mixtures, using both chemical oxidation with iodine and electrolytic

oxidation to produce the cations. Due to the complexity of their hyperfine spectra, studies were possible only in the region of fast exchange.

By using the dibenzo-p-dioxin (DBDO) cation system, from which one can obtain a well resolved five-line hyperfine spectrum, we were able to make rate measurements in the region of slow exchange as well as the region of fast exchange. Second order rate constants obtained from the region of fast and slow exchange could then be compared. An investigation into the validity of the correction factor in equation (6) for cation systems as was done by Zandstra and Weissman³⁶ for anion systems was also performed.

II. EXPERIMENTAL PROCEDURES

1.) PREPARATION AND PURIFICATION OF CHEMICALS USED

A. SUBSTANCES STUDIED

Tri-p-tolylamine (TPTA) was prepared by the method of Walter.³⁷ The product obtained from the above method contained oily by-products along with the tertiary amine. This black impurity was removed by several recrystallizations from glacial acetic acid and then vacuum sublimed at its melting point. White crystals with melting point of 116.5 to 117.5 degrees centigrade were obtained and used in the rate studies.

Phenothiazine (PTAZ) and dibenzo-p-dioxin (DBDO) were commercially obtained and vacuum sublimed. Reagent grade iodine and tetra-n-butylammonium perchlorate (TBAP) were used as commercially obtained. Commercially obtained triple distilled mercury was used in electrochemical experiments.

B. SOLVENTS

Reagent grade chloroform was purified by removing the ethanol with concentrated sulfuric acid and then washing several times with water. Distillation from P_2O_5 keeping the center fraction, followed by storage in a vacuum bottle over type 4Å molecular sieves completed its purification. Reagent grade acetonitrile was twice distilled from P_2O_5 and the center cut portion was stored in a vacuum bottle