

# Spin-Spin and Electron-Exchange Rates of Radicals and Radical Ions

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**Abstract:** The spin-spin exchange rates for several organic free radicals in solution have been measured. These rates have been compared to the electron-transfer rates for systems involving the same radicals. The rates for the spin-spin interactions appear to be controlled purely by diffusion, while the electron-transfer rates differ significantly among themselves and from the spin-spin rates.

A study of the spin-spin interaction of free radicals in dilute solution has been undertaken. The radical systems,  $K_2NO(SO_3)_2$  and potassium naphthalenide, have been examined previously.<sup>1,2</sup> It is well known that such spin-spin interactions will lead to the broadening of the lines of the hyperfine components of the electron paramagnetic resonance (epr) spectra of the species. Both studies indicated that this broadening was a linear function of the radical concentration (for moderately dilute concentrations) and that second-order rate constants for the interaction could be derived from the slopes of line width *vs.* concentration plots. In each case the rate constants derived were slightly greater than  $10^9$  but differed in a manner not readily explainable by viscosity or Coulombic arguments based on diffusion theory.

A similar intermolecular process is homogeneous electron exchange (herein designated as electron transfer) in which a molecule with an unpaired electron interacts with an identical (parent) molecule without an unpaired electron. It has been shown that a number of factors, solvation, ion pairing, and substituents, have a marked effect on the electron-transfer rates.<sup>3-7</sup> It has been the purpose of this study to determine if such effects are also reflected in the spin-spin exchange rates or if all spin-spin interactions are essentially controlled by diffusion.

## Experimental Section

The electron-transfer rates were measured from line broadening as previously described.<sup>6,7</sup> The spin-spin exchange rates were measured in the same manner except that concentration of radical was varied rather than that of parent.

The stable di-*t*-butylnitroxide (DTBN) radical was prepared and purified following the procedure of Hoffmann, *et al.*<sup>8,9</sup> The other radicals were generated electrochemically by rather standard procedures.<sup>10</sup> The solvent was dimethylformamide (DMF) with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte. The DMF was dried over calcium hydride and distilled from phthalic anhydride. The other chemicals were either Eastman White Label or purified by standard techniques.

- (1) M. T. Jones, *J. Chem. Phys.*, **38**, 2892 (1963).
- (2) J. C. Danner and T. R. Tuttle, *J. Am. Chem. Soc.*, **85**, 4052 (1963).
- (3) R. L. Ward and S. I. Weissman, *ibid.*, **79**, 2086 (1957).
- (4) S. I. Weissman, *Z. Elektrochem.*, **64**, 47 (1960).
- (5) P. J. Zandstra and S. I. Weissman, *J. Chem. Phys.*, **35**, 757 (1961).
- (6) T. Layloff, *et al.*, *Nature*, **205**, 382 (1965).
- (7) P. A. Malachuk, T. A. Miller, T. Layloff, and R. N. Adams, *Proc. IAEA Symp. Electron Exchange, Brookhaven, N. Y., 1965*, 157 (1965).
- (8) A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).
- (9) A. K. Hoffmann, *et al.*, *ibid.*, **86**, 639 (1964).
- (10) R. N. Adams, *J. Electroanal. Chem.*, **8**, 151 (1964).

There are problems inherent in the electrochemical generation of the radicals. The species are usually not quantitatively transformed to the paramagnetic forms and the paramagnetic forms may be relatively unstable. To eliminate these difficulties the radical concentrations were determined directly from the epr spectra. Under appropriate conditions, proper modulation amplitude, line widths, etc., a simple extension of the theory<sup>7,11,12</sup> derived to measure widths of lines broadened by homogeneous exchange shows that

$$A^2/I \propto X$$

where  $A$  = the area under the positive portion of the first derivative curve of the epr signal,  $I$  = the intensity of the derivative curve,  $X$  = quantity of radical "seen" by the epr spectrometer.

The quantity of radical "seen" by the spectrometer is naturally directly proportional to the radical concentration if other parameters, position of cell in the microwave cavity, signal level, etc., are held constant. In these studies these factors were held constant by means of a flow system through the cavity.  $A^2/I$  measurements were calibrated by known concentrations of the stable DTBN radical.

## Results

The spin-spin and electron-transfer rates are listed in Table I. The experimentally derived values of the spin-spin rate constants were multiplied by a factor of 2 to obtain the bimolecular rate constants listed in Table I for encounters between free-radical species. The values in parentheses for potassium naphthalenide and  $K_2NO(SO_3)_2$  are rate constants extrapolated from literature data which would be predicted in DMF on the basis of viscosity differences provided the exchange is diffusion controlled.

Table I

Compound	Spin-spin rate <sup>a</sup>	Electron-transfer rate <sup>a</sup>
DTBN	$7.5 \times 10^9$	...
Potassium naphthalenide	$5.6 \times 10^9$ <sup>b</sup> ( $3.2 \times 10^9$ )	$5.7 \times 10^7$ <sup>b</sup>
<i>p</i> -Benzoquinone	$2.0 \times 10^9$	$3.8 \times 10^8$
Nitrobenzene	$3.6 \times 10^9$	$3.0 \times 10^7$
Tetramethyl- <i>p</i> -benzoquinone	$3.0 \times 10^9$	$6.2 \times 10^7$
$K_2NO(SO_3)_2$	$3.1 \times 10^9$ <sup>c</sup> ( $3.9 \times 10^9$ )	...

<sup>a</sup> Second-order rate constants in l./mole sec. <sup>b</sup> Determined in tetrahydrofuran.<sup>2,3</sup> <sup>c</sup> Determined in buffered aqueous solution.<sup>1</sup>

- (11) T. Layloff, Ph.D. Thesis, University of Kansas, 1964.
- (12) T. A. Miller, *Search*, **5**, 16 (1965).

Theoretically there is considerable question as to the validity of using the factor of 2 in this conversion.<sup>13</sup> We are unable to decide this question and pending a definitive theoretical interpretation have included it in the calculation. This factor in no way impairs the qualitative or quantitative conclusions reached in this study. In passing it may be noted that the bimolecular rate constant can be predicted by the Smoluchowski theory of diffusion rates by substituting the Stokes-Einstein relationship for the diffusion coefficient.<sup>14</sup> For DTBN the predicted rate is  $8.3 \times 10^9$  l./mole sec which compares with the experimental value in Table I of  $7.5 \times 10^9$  l./mole sec (which includes the factor of 2). Considering the crudeness of the Stokes-Einstein relation, the agreement is surprisingly good, but may be fortuitous and cannot be advanced as an argument in favor of the calculation.

The approximately 80% variation of the spin-spin rate constants of the mononegative species is of little significance. Errors of 20-30% are introduced in these rate constants from the concentration and line-width determinations owing to both the intrinsic lack of precision in area measurements and the changing line shapes at these concentrations. The important point we wish to make is that it appears that the spin-spin rates of a wide variety of organic radicals are

(13) M. T. Jones, private communication.

(14) E. F. Caldin, "Fast Reactions In Solution," Blackwell Scientific Publication, New York, N. Y., 1964.

purely diffusional controlled (at least over a moderately dilute concentration range, *ca.*  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  M). However, the electron-transfer rates for these same compounds vary by over an order of magnitude.

In the spin-spin case there must exist considerable overlap of the wave functions of the unpaired electrons. For the electron-transfer reaction there must be overlap of the wave functions of the unpaired electron and the acceptor molecule. From the similarity of the spin-spin rates it is seen that the frequency of occurrence of such overlaps is approximately the same for all molecules in question. Thus, it would appear that retardation of the electron-transfer rates by steric, solvent, and substituent effects is not due to any alteration in the probability of collisions which have wave function overlap. Instead, the retardation is caused by the reorganization energy associated with charge transfer in the electron-transfer process. This intuitive argument seems to be substantiated by the experimental data.

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## The Interaction of Chain Molecules Carrying Reactive and Catalytic Chain Substituents<sup>1</sup>

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**Abstract.** The hydrolysis of acrylamide (A) and dimethylacrylamide (D) copolymers with *p*-nitrophenyl acrylate (NA) and *p*-nitrophenyl N-acrylyl-6-aminocaproate (NAC) was studied in the presence of catalytic copolymers of 4-vinylimidazole (VI) or N-acrylylhistamine (AH). Copolymers of VI did not catalyze the solvolysis of copolymers of NA, presumably because steric hindrance is prohibitive when both interacting groups are close to the chain backbone. Copolymer A-AH did not catalyze the solvolysis of copolymer A-NA in water but was catalytically active in 40% aqueous methanol, a relatively poor solvent medium. The reaction of A-NAC catalyzed by A-AH followed first-order kinetics in water solution and the rate was independent of the molecular weight of the A-AH used. This suggests that shielding of the reactive groups by the macromolecular coil is negligible under the conditions employed. In water-methanol solution the reaction exhibited slight but significant deviation from first-order kinetics. In experiments involving D-NAC with A-AH and D-AH, the expected specificity in favor of interaction of reactive groups attached to similar polymer backbones was not observed.

In the selection of methods for the study of polymer solutions, little use has been made, so far, of the possibilities inherent in studies of the chemical reactivity of dissolved chain molecules. Yet, a recent survey of this field<sup>2</sup> leads to the conclusion that such

(1) Abstracted from the Ph.D. thesis submitted by W. R. Song to the Graduate School of the Polytechnic Institute of Brooklyn in June 1965. Financial support of this work by Grant GM-05811 of the National Institutes of Health is gratefully acknowledged.

methods may supplement the more usual physicochemical techniques to yield information which may not be attainable by other means.

Consider a system represented schematically in Figure 1 in which a solution contains two types of chain molecules. The backbones of these chain

(2) H. Morawetz, "Macromolecules in Solution," Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1965, Chapter IX.