gen atoms. In the activated complex the symmetric stretching and bending vibrations must be considered, the asymmetric vibration being assumed similar to the reaction coördinate motion and, therefore, having given rise to μ. Since the reactant state is represented by a two- and the transition state by a three-center model, the argument presented above concerning comparison between a normal mode of the reactant state model and the assumed reaction coördinate motion is applied in a different sense, *viz.*, that correspondence is sought between the latter and a normal vibrational mode which the activated complex would exhibit *if* the vibration leading to increase in the reaction coördinate were ordinary. By juggling the properties of the C–O–Pb system one can produce agreement with the temperature dependence of k_4/k_5 using a group of force constants and distances having reasonable magnitudes, provided that the asymmetric normal mode is selected as the reaction coördinate motion.

An alternate choice for the process leading to C–C bond rupture is asymmetric motion in the three-center system C–C–O, bond extension taking place between C and C, and bond formation between C and O. In effect this adds still another parameter to the over-all picture, *i.e.*, p for this triad, and does not further illuminate the situation.

In Table I the total change in $R^0_{CO_2}$ is only $(11 \pm 5) \times 10^{-6}$; for none of the models considered above is the change predicted in O^{18} content of product carbon dioxide outside the limits defined by this figure. Thus the O^{18} isotope effect is not a useful adjunct to evaluation of these models.

Acknowledgment.—We are indebted to Mrs. Beverly Thomas for the mass spectrometric determinations, and to Professor H. S. Gutowsky and Dr. Martin Karplus for stimulating discussion. Dr. James Y. Tong and the staff of the University of Illinois Digital Computer Laboratory have performed calculations which permitted checking of several ideas. This research was sponsored by the U. S. Atomic Energy Commission.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE WASHINGTON UNIVERSITY]

Electron Spin Resonance Study of the Electron Exchange between Naphthalene Negative Ion and Naphthalene[1]

BY R. L. WARD[2] AND S. I. WEISSMAN

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The rate of the electron exchange reaction between naphthalene negative ion and naphthalene has been determined by a spectroscopic method. Broadening of the electron spin resonance lines of naphthalene negative ion occurs in the presence of naphthalene. Bimolecular rate constants are deduced from the variation of line breadth with concentration of added naphthalene. The rate constants vary with solvent and with the choice of positive ion. They lie in the range 10^7–10^9 liter mole^{-1} sec.$^{-1}$.

Introduction

The rate of a chemical reaction is usually determined by a sequence of measurements in time of properties which vary as the reaction proceeds. Such measurements yield directly the net changes in the quantities of reactants and products. Individual rates of production and consumption are inferred from the net rates and these inferred rates are sometimes subject to considerable uncertainties. Direct determination of rates of production and consumption of participants in a reaction has become possible in certain cases by the recent development of radiofrequency and microwave spectroscopic techniques of high resolving power.

The measurements depend on the fact that the shape of a spectroscopic line associated with a transition between a pair of states is affected by the mean life of the states. The essential ideas involved in the relations between lifetimes and line breadths were worked out by Lorentz in his treatments of the effects of collisions on the breadth of spectral lines.[3] Many authors have further developed the subject.[4–11] The theoretical treatment of P. W. Anderson[8a] appears to be the most readily applicable to the interpretation of the kinds of experiments which we shall describe here.

These experiments consist of observations of the electron spin resonance spectra of naphthalene negative ion (to be referred to as naphthalenide) in the presence of naphthalene.

In the concentration range 10^{-4}–10^{-3} M in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), the spectrum of naphthalenide consists of a set of seventeen hyperfine components extending over a field interval of 27.2 oersteds. The breadth of each line is about 0.9 oersteds between points of extreme slope. This description applies to the spectrum of lithium, potassium, rubidium or cesium naphthalenide. Sodium naphthalenide, on the other hand, behaves differently. In DME its spectrum is

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[1] This research was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] E. I. du Pont de Nemours Post-Graduate Fellow, 1955–1956.

[3] H. A. Lorentz, *Proc. Acad. Amst.*, **8**, 591 (1906).

[4] (a) V. Weisskopf, *Z. Physik.*, **75**, 287 (1932); (b) J. H. Van Vleck and V. Weisskopf, *Rev. Mod. Phys.*, **17**, 227 (1945).

[5] H. M. Foley, *Phys. Rev.*, **69**, 616 (1946).

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[7] P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.*, **25**, 269 (1953).

[8] (a) P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 316 (1954); (b) R. Kubo and K. Tomita, *ibid.*, **9**, 888 (1954).

[9] D. Pines and C. P. Slichter, *Phys. Rev.*, **100**, 1014 (1955).

[10] J. T. Arnold, *ibid.*, **102**, 136 (1956).

[11] H. McConnell and H. Weaver, *J. Chem. Phys.*, **25**, 307 (1956).

similar except for a markedly greater line breadth to that of the other salts, while in THF it is completely different in structure.[12] At concentrations lower than 10^{-5} M the normal spectrum of seventeen lines is further resolved into one of twenty-three lines. The contribution of each of the protons in naphthalenide to the hyperfine splitting has been determined.[12]

As naphthalene is added to a solution of naphthalenide, a broadening of the hyperfine components of the ion occurs.[13] As more naphthalene is added, the lines merge into a single broad band which in some cases continues to broaden with further addition of naphthalene and in others becomes narrower. From the broadening at the lower concentration of added naphthalene a rate constant for the electron exchange reaction between naphthalene and naphthalene negative ion may be obtained.

Experimental Methods

Solutions of naphthalenide salts were prepared in high vacuum by methods already described.[14] The apparatus included a tube which could be inserted into the cavity of the electron spin resonance spectrometer and an optical absorption cell which could be used with a Cary or Beckman spectrophotometer. The optical and electron spin resonance spectra of the solution were observed before and after addition of naphthalene. The concentration of naphthalenide was determined from the optical spectra through the use of the extinction coefficients measured by Paul.[15] The optical spectrum served as a check of the purity of the naphthalenide solution.

The electron spin resonance spectra were recorded immediately before and after addition of the naphthalene under identical conditions of cavity tuning, modulation and amplification. The spin resonance spectra were measured at nine thousand megacycles in a spectrometer designed and constructed by Professor J. Townsend.

When small amounts of naphthalene were used they were introduced as aliquots of a solution in cyclohexane of known concentration. The cyclohexane was removed by distillation. When large amounts of naphthalene were required, they were purified and introduced into the apparatus by the methods described by Paul. The naphthalene was contained in an evacuated side arm separated from the rest of the apparatus by a break seal. The concentration of naphthalene, when it could not be added in known amount at the beginning of the experiment, was determined by analysis after completion of the spectroscopic measurements.

Results and Discussion

The small broadenings of the hyperfine components which occur at low naphthalene concentrations are not easily determined by direct measurement of line width. They are better determined indirectly from the intensities of the lines. The spin resonance spectra were recorded as derivative of absorption X'' with respect to magnetic field H against the field. It may be shown that the intensity of a single peak as measured by the difference in values of $\mathrm{d}X''/\mathrm{d}H$ at maximum and minimum varies inversely as the square of the line breadth, provided the shape of the line remains unchanged, *i.e.*, that the absorption may be represented by a single function of field $X''[(H - H_0)/\delta H]$ where H_0 is the field at the center of the line and δH is a line breadth. In addition, the intensity of the line depends on the number of free radical molecules in the cavity, the Q and filling factor of the cavity, the amplitude of modulation and the amplification. These parameters, with the exception of the number of free radical molecules in the cavity, were kept constant in each of our experiments. The number of free radical molecules in the cavity decreased slightly when naphthalene was added to a solution because of dilution and because of occasional decomposition of free radical by impurities in the naphthalene. This decrease was determined in each experiment from the optical absorption spectrum. Correction for it was made in the treatment of the data.

Typical examples of the observed effects are given in Figs. 1–3. In each case, $\mathrm{d}X''/\mathrm{d}H$, the derivative of absorption with respect to field is plotted as a function of field H. In Fig. 1 is shown the effect of addition of naphthalene at 0.103 M to a solution of potassium naphthalenide 1.36×10^{-3} M in THF. A small broadening results. It is observed in two ways. The intensities of the individual peaks are reduced and the resolution of adjacent peaks is diminished. While the derivative changes signs between all pairs of adjacent peaks in the unbroadened spectrum, it does not do so in the broadened spectrum.

In Fig. 2 is shown the effect of addition of naphthalene at 0.218 M to a solution of potassium naphthalenide at 1.4×10^{-3} M in DME. An example of exchange narrowing is shown in Fig. 3.

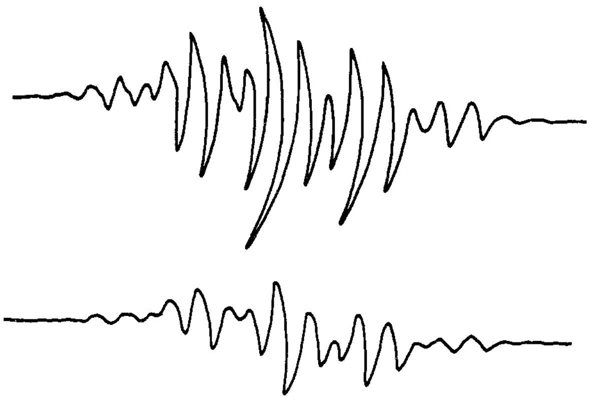

Fig. 1.—Spin resonance spectrum of 1.36×10^{-3} M potassium naphthalenide in THF: above, no added naphthalene; below, naphthalene added at 0.103 M.

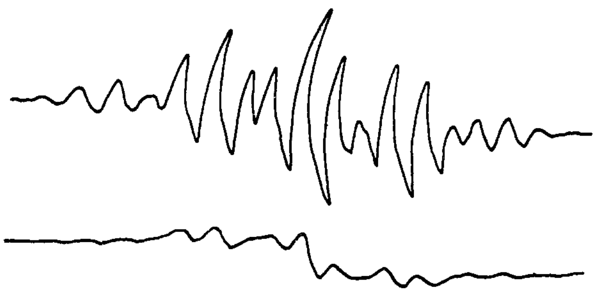

Fig. 2.—Spin resonance spectrum of 1.4×10^{-3} M potassium naphthalenide in DME: above, no added naphthalene; below, naphthalene added at 0.218 M.

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[12] T. R. Tuttle, R. L. Ward and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

[13] R. L. Ward and S. I. Weissman, THIS JOURNAL, **76**, 3612 (1954).

[14] D. E. Paul, D. Lipkin and S. I. Weissman, *ibid.*, **78**, 116 (1956).

[15] D. E. Paul, Ph.D. thesis, Washington University, 1954.

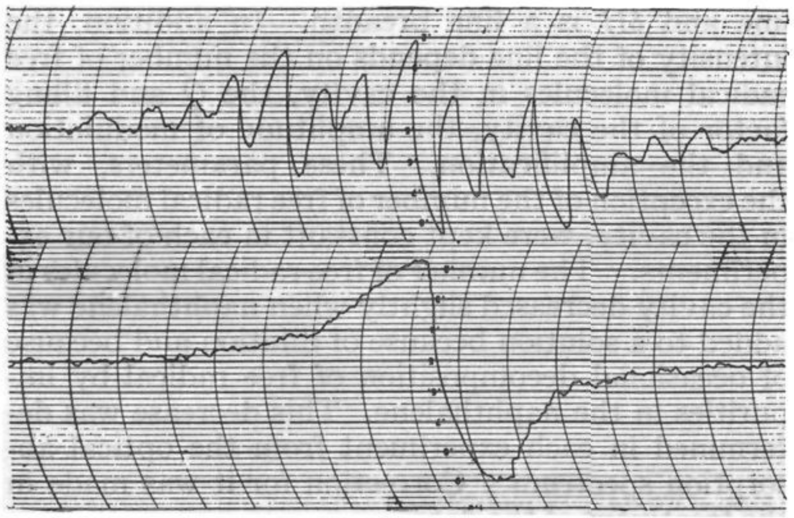

Fig. 3.—Spin resonance of 1.0×10^{-3} M lithium naphthalenide in THF: above, no added naphthalene; below, naphthalene added at 0.405 M.

Here naphthalene at 0.405 M was added to a solution of lithium naphthalenide at 1.0×10^{-3} M in THF.

From the spectra, of which those described in the preceding paragraph are typical, we wish to deduce information concerning the electron exchange reaction. We assume that in the region of small line broadenings (broadenings small compared with the separation betweeen lines), the contributions to the line breadth from individual broadening mechanisms are additive. This assumption corresponds to the more familiar one of additivity of rates.

We write, then, for the breadth of a line $\delta H = \delta H_0 + \delta H_N$ where δH_0 is the breadth in the absence of added naphthalene and δH_N is the contribution to the breadth from the electron exchange reaction with the added naphthalene. The ratio of intensity $I(\mathrm{N})$ at concentration of added naphthalene N to the corresponding intensity $I(0)$ before naphthalene has been added is given by

$$\frac{I(\mathrm{N})}{I(0)} = \frac{(\delta H_0)^2}{(\delta H_0 + \delta H_\mathrm{N})^2} \qquad (1)$$

A convenient form of this relation for our purposes is

$$\sqrt{\frac{I(0)}{I(\mathrm{N})}} = 1 + \frac{\delta H_\mathrm{N}}{\delta H_0} \qquad (2)$$

For further analysis we assume that the lines are Lorentzian. The work of Lloyd and Pake[16] has shown that in dilute solutions of the free radical peroxylamine disulfonate the lines are close to Lorentzian and that their breadth is accounted for by thermal relaxation processes. Anderson's[8a] work has shown that in the region of small broadening, exchange reactions also produce Lorentzian lines.

For a Lorentzian line the field dependence of absorption is given by

$$X'' = \frac{X''_{\max}\delta H^2}{\delta H^2 + (H - H_0)^2}$$

where $X''_{\max}$ is the intensity at the maximum, H_0 the field at the center of the line and δH the half width of the line at half maximum absorption. H in oersteds is related, for a pure electron spin resonance of the type studied here to the frequency V by

$$V = \frac{g\mu_0 H}{h} = 2.83 \times 10^{6} H$$

g is the spectroscopic splitting factor for an electron spin, μ_0 is the Bohr magneton, h Planck's constant.

Anderson's theory which is based on a frequency modulation model (as well as the theories based on the Bloch equations) indicate that in the region of line broadenings small compared with the separation between lines, the contribution to the line breadth δV of the exchange process is given by

$$\frac{1}{\tau} = 2\pi\delta V \qquad (3)$$

where τ is the mean time between electron exchanges, and δV is the half width at half maximum. In Anderson's theory the assumption is made that *the exchange process is Markoffian.*[17] This assumption seems to be a reasonable one. We should emphasize Anderson's result that the lines are Lorentzian with contributions to the breadth δV given by the last equation only when the mean frequency of exchange $1/\tau$ is small compared with $V_\mathrm{i} - V_\mathrm{j}$ where V_i and V_j are the frequencies of adjacent lines. When $1/\tau > V_\mathrm{i} - V_\mathrm{j}$ exchange narrowing may occur.

In naphthalene negative ion each line in the spectrum arises from an electron spin transition in a molecule of specified proton spin quantum numbers. Although there are eight protons, because of symmetry only two proton quantum numbers—M_α, the sum of the projections on the field of the spins of the α protons, and M_β, a similar sum for the β protons—fix the position of the electron spin resonance line. When the electron jumps from one naphthalene to another, it usually finds different values M_α, M_β in the second site from the first.

The central peak in the hyperfine pattern of naphthalene negative ion arises from electron spin transitions in molecules with $M_\alpha = M_\beta = 0$. This peak is the most intense one in the spectrum and it is single. The data to be presented in the following paragraphs are obtained almost exclusively from this peak.

If τ_{N^-} is the mean time between exchanges for a naphthalene negative ion, and τ_N the corresponding time for naphthalene, for a bimolecular exchange where k is the rate constant and (N) and (N$^-$) are concentrations of naphthalene and naphthalene negative ion

$$\frac{(\mathrm{N}^-)}{\tau_{\mathrm{N}^-}} = \frac{(\mathrm{N})}{\tau_\mathrm{N}} = k(\mathrm{N})(\mathrm{N}^-)$$

Hence

$$\frac{1}{\tau_{\mathrm{N}^-}} = k(\mathrm{N}); \quad \frac{1}{\tau_\mathrm{N}} = k(\mathrm{N}^-)$$

If ΔH_N is the line breadth as measured between points of extreme slope

$$\frac{1}{\tau_{\mathrm{N}^-}} = (2\pi)(2.83 \times 10^6)\frac{\sqrt{3}}{2}\Delta H_\mathrm{N} = k(\mathrm{N})$$

($\sqrt{3}/2$ is the proportionality factor between half width at half maximum and width between points of extreme slope.) We then find a relationship between the line breadth (between points of extreme

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[16] J. P. Lloyd and G. E. Pake, *Phys. Rev.*, **94**, 579 (1954).

[17] An essential feature of a Markoffian process is that the probabilities of transition at a given time do not depend on past history.

slope) produced by exchange, ΔH_N, and the second-order rate constant

$$k = \sqrt{3}\,\pi\,2.83 \times 10^6 \frac{\Delta H_N}{(N)} \qquad (4)$$

From (2) and (4) we find

$$\sqrt{\frac{I(0)}{I(N)}} = 1 + \frac{k(N)}{\sqrt{3}\pi\,2.83 \times 10^6 \Delta H_0}$$

In the curves given in Figs. 4–8 we plot the measured values of $\sqrt{I(0)/I(N)}$ against $(N)/\Delta H_0$. ΔH_0 in each case was found from direct measurement of the central line before naphthalene was added. Each point represents a separate preparation of naphthalenide and addition of naphthalene to it.

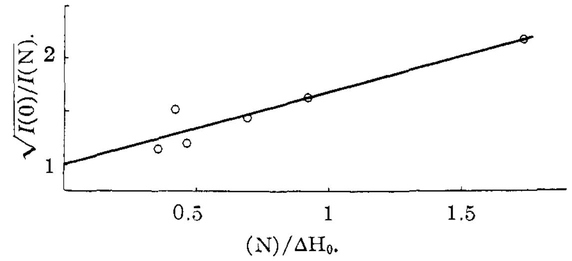

Fig. 4.—$\sqrt{I(0)/I(N)}$ *vs.* $(N)/\Delta H_0$ for sodium naphthalenide in THF.

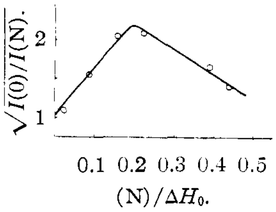

Fig. 5.—$\sqrt{I(0)/I(N)}$ *vs.* $(N)/\Delta H_0$ for potassium naphthalenide in DME.

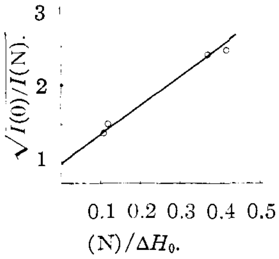

Fig. 6.—$\sqrt{I(0)/I(N)}$ *vs.* $(N)/\Delta H_0$ for potassium naphthalenide in THF.

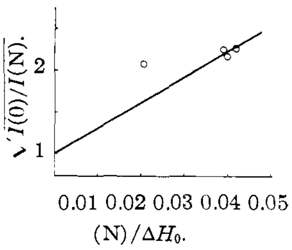

Fig. 7.—$\sqrt{I(0)/I(N)}$ *vs.* $(N)/\Delta H_0$ for lithium naphthalenide in THF.

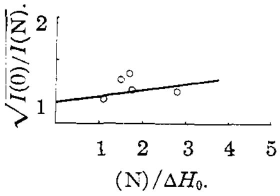

Fig. 8.—$\sqrt{I(0)/I(N)}$ *vs.* $(N)/\Delta H_0$ for sodium naphthalenide in DME.

A second-order rate constant is determined from the slope of the curve at low concentration of added naphthalene.

A summary of the rate constants for the exchange for the various combinations of cation and solvent used in these experiments is given in Table I.

All the experiments summarized in Table I were at temperatures between 30 and 35°. Several experiments were performed with the lithium and potassium salts in tetrahydrofuran at −70° and one was performed with the sodium salt in THF at 60°. All showed no observable effects of temperature. Because our apparatus was not well suited for reliable measurements at these temperatures, a rough upper limit of 2600 cal. mole^{-1} was established for the activation energy.

The reasons for the dependence of rate on the nature of the cation are not clear to us. It will be noticed that the rate constant for the sodium salt in dimethoxyethane is much higher than for the potassium salt. The following experiments were performed in connection with this point. To a solution of potassium naphthalenide in 1,2-dimethoxyethane was added naphthalene at 1.3×10^{-2} *M*. This concentration produces little broadening for the potassium salt. To the solution containing potassium naphthalenide and naphthalene, a large excess (0.22 *M*) of sodium iodide was added. A barely perceptible broadening occurred. In another experiment naphthalene at 1.8×10^{-2} *M* was added to sodium naphthalenide at 0.96×10^{-3} *M* in DME to produce an easily observed broadening. To this solution 1.8×10^{-3} *M* potassium iodide was added. The spectrum reverted to the unbroadened spectrum of the potassium salt. This set of spectra is shown in Fig. 9.

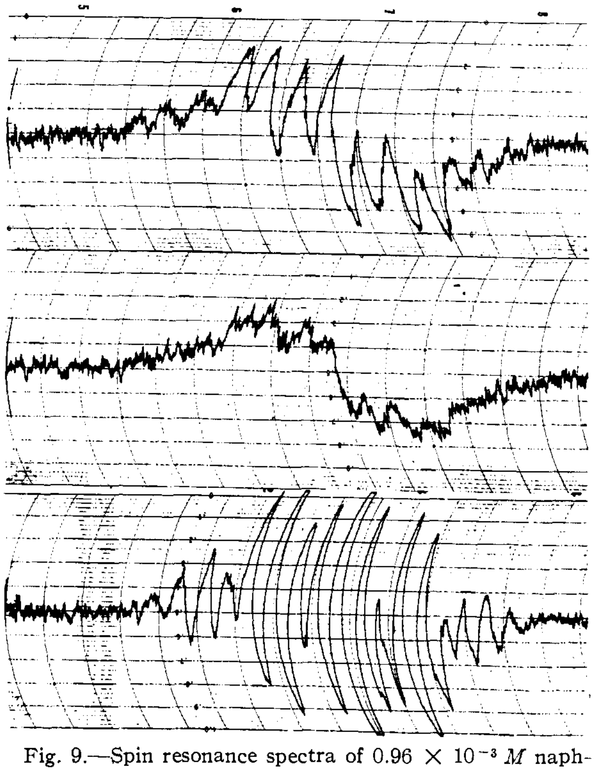

Fig. 9.—Spin resonance spectra of 0.96×10^{-3} *M* naphthalenide in DME: above, pure sodium salt; center, naphthalene added at 1.8×10^{-2} *M;* below, potassium iodide at 1.8×10^{-3} *M* added to solution which had given center spectrum.

The two experiments show that the state of the solution is independent of the order of adding of reagents. While other interpretations are possible, the experiments are consistent with the statement that the rapid exchange of the sodium salt proceeds through ion pairs and that the equilibrium constant for the reaction

$$Na^+C_{10}H_8^- + KI = Na^+I^- + K^+C_{10}H_8^-$$

is at least 10^4.

TABLE I

RATE CONSTANTS FOR ELECTRON TRANSFER BETWEEN NAPHTHALENIDE ION AND NAPHTHALENE

Positive ion	Solvent	k (l. mole^{-1} sec.$^{-1}$)
K^+	DME	$(7.6 \pm 3) \times 10^7$
K^+	THF	$(5.7 \pm 1) \times 10^7$
Na^+	DME	$(1 +3 -0.7) \times 10^9$
Na^+	THF	$(1 +3 -0.6) \times 10^7$
Li^+	THF	$(4.6 \pm 3) \times 10^8$

There are a few points concerning interpretation of the results which may be further discussed. One involves the possibility that the formation of stable complexes between naphthalene negative ion and naphthalene is responsible for the observed phenomena. Such a possibility is contradicted by several observations. First, no observable change in the optical spectrum of naphthalenide occurs even in the presence of a thousand-fold excess of naphthalene. Second, if a stable complex were formed, a superposition of the electron spin resonance spectra of the complex and the uncomplexed species would be expected. No sign of such superposition is observed. Third is the fact that the electron spin resonance spectrum changes continuously over the entire concentration range of added naphthalene.

Another question is involved in the following. Do all electron jumps contribute to the broadening? If they do not our rate constants are too low since they fail to include some jumps. There is little question that jumps in which the values of M_α, M_β in the final site differ from those in the original site lead to broadening. But for those jumps in which the initial and final values of M_α, M_β are equal, the answer is not certain. Broadening could occur in two ways in this case. A change in the direction of electron spin accompanying the jump will lead to broadening. Whether such a change occurs depends on the detailed nature of the jump—on the spectrum of the magnetic disturbance accompanying it. A direct experimental answer by measurement of thermal relaxation times is possible but difficult. Until such measurements are made we can surmise that in those cases in which the lines continue to broaden as naphthalene is added, changes of direction in spin are likely to accompany electron jumps, while in those cases in which the lines exhibit narrowing at high concentrations of added naphthalene such changes do not occur.

A second way in which jumps between sites of the same M_α, M_β could lead to broadening involves a change in phase of the motion of the electronic moment without change in direction of spin. A classical description of the problem similar to one given by McConnell and Weaver[11] is the following. If the phase of the Larmor precession of the electron spin at some instant after the jump differs by an appreciable fraction of a radian from the value it would have had at that instant if the jump had not occurred, broadening results. If V_0 is the frequency in the site between which the jumps occur, V^* the average frequency in transit, and τ the time spent in transit, the condition for broadening is

$$\tau > \left| \frac{1}{V_0 - V^*} \right|$$

In the cases studied by us it is unlikely that $V^* - V_0$ would be greater than 10^8 or 10^9 cycles per second (50–500 oersteds). (A value of 10^9 cycles would correspond to a very severe magnetic perturbation during the transition.) Hence transit times of order of 10^{-9} to 10^{-8} second would be required for broadening. If such long times were spent in transit, an appreciable fraction of the electrons would always be in transit at the higher concentrations of added naphthalene. No sign of such behavior is found in the optical spectra of the solutions. Hence it appears that broadening associated with changes in phase of the motion of the electron spin during jumps between sites of the same M_α, M_β are not significant.

We may estimate the error in our rate constants if such jumps do not contribute to the broadening. For the eight protons in naphthalene there are 256 spin states. The lines at the high and low field extremes ($M_\alpha = M_\beta = \pm 2$) of the spectrum may each be achieved in only one of these ways, while the intense center line ($M_\alpha = M_\beta = 0$) may be achieved in seventy different ways. Thus 255 of the 256 electron jumps originating in one of the extreme lines terminate in a frequency different from the original one, while 196 of 256 jumps originating in the central line terminate in a different frequency. Use of the central line may underestimate the exchange rate by about 27%—not a very serious error in the present state of the measurements.

Comparison between exchange rates as measured by the line broadening method and those measured by the isotope tracer method would be very valuable. Because of the difficulties attendant upon handling the very reactive free radicals used in our experiment, and because of the rapid exchanges, a tracer method does not seem feasible. However, in certain other rapid exchanges, especially those studied by Wahl and his collaborators, it may be possible to study the reactions by both methods.

ST. LOUIS, MISSOURI