

Heisenberg spin exchange and chemical electron exchange in naphthalene negative ion—An electron spin-lattice relaxation study

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Abstract. Electron spin-lattice relaxation times (T_{1e}) as determined by saturation recovery technique and linewidths have been investigated as a function of the concentration of naphthalene anion and the unreduced naphthalene in dimethoxyethane from conditions of slow exchange to fast exchange. It was observed that Heisenberg spin exchange was more effective in determining T_{1e} and linewidth than chemical exchange at comparable concentrations. Contrary to earlier findings, T_{1e} was found to depend on the radical concentration even at the fast exchange regime.

Keywords. Electron spin-lattice relaxation; ESR; chemical exchange; Heisenberg exchange; aromatic anions; naphthalene negative ion; saturation recovery technique.

1. Introduction

During our current systematic study of the electron spin lattice relaxation times (T_{1e}) of aromatic negative ions by the saturation recovery technique, we have made some interesting observations on the dependence of T_{1e} on the concentration of the radical anions. It has been recognised for several years that intermolecular electron spin exchange reactions between radicals (Heisenberg exchange) and electron exchange between the radical and their diamagnetic precursors (chemical exchange) are relaxation mechanisms and contribute to ESR linewidths and T_{1e} 's (Anderson 1954; Ward and Weissman 1957; Piette and Anderson 1959; McConnell 1958; Swift and Connick 1962; O'Reilly and Poole 1963; Sohma 1962; Freed 1967). The rate of chemical exchange between naphthalene anion and neutral naphthalene has been determined as early as 1957 by a study of the dependence of ESR linewidth on the concentration of the neutral species (Ward and Weissman 1957). Similar studies on sulphur radical have been reported (Gardner and Fraenkel 1956). However, the effect of such chemical and Heisenberg exchange on T_{1e} has been poorly understood.

In our laboratory it has been demonstrated that T_{1e} of semiquinone, as measured by saturation recovery technique, are independent of the free radical concentration in alcoholic solvents but strongly dependent on the radical concentration in aprotic solvents such as acetonitrile and tetrahydrofuran (Rengan *et al* 1974a, b). This observation was presumed to indicate the presence of a solvent cage around the free radical due to hydrogen bonding in alcohols leading to decreased probability of encounter between free radicals; at similar concentrations of free radicals, the rate of intermolecular encounters is normal when the solvent cage is absent in the aprotic solvents. Cheng and Weissman (1976) have measured T_{1e} 's in solutions of potassium tetracyanoethylene containing neutral tetracyanoethylene (TCNE) by progressive

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saturation technique. These studies paralleled those of Eastman *et al* (1969) wherein the stress was on the study of Heisenberg spin exchange between TCNE^- radicals, rather than chemical exchange. Percival and Hyde (1976) have attributed the concentration dependence of T_{1e} of nitroxides to electron-electron dipolar coupling modulated by translational diffusion. They conclude that Heisenberg spin exchange, which makes an important contribution to the linewidth, is a pseudo-secular process and thus does not affect T_{1e} . Owing to the paucity of data on longitudinal relaxation times, T_{1e} , our understanding of the effect of Heisenberg and chemical exchanges on T_{1e} is rather poor. The conclusions reached with T_{1e} determined by progressive saturation technique, are circumspect since the quantity measured experimentally by the CW technique is T_{1e}^{eff} , which includes contributions from various pseudo-secular processes (Percival and Hyde 1976). In the pulsed saturation recovery method, which is being practised by only a few groups (Rengan *et al* 1974; Percival and Hyde 1976; Fessenden *et al* 1981), T_{1e} is measured directly.

The effect of Heisenberg and chemical exchange is manifested most dramatically in the linewidths of ESR spectra. In the slow exchange regime, both of the exchanges broaden first the individual hyperfine lines. With the increase of exchange rates, all the hyperfine lines merge to a single broad line. With further increase of exchange rate, the broad line starts narrowing and at extremely high rate, a single exchange narrowed Lorentzian line results. Freed and coworkers (Eastman *et al* 1969) have shown experimentally and theoretically that in the slow exchange regime T_{1e}^{eff} of TCNE^- decreases with increase in concentration of the radical. Cheng and Weissman (1976) conclude that in the case of slow exchange between K^+ TCNE^- and TCNE , T_{1e}^{eff} decreases with increase of TCNE concentration and that in the fast exchange regime $1/T_2$ is proportional to the reciprocal of the concentration of TCNE while T_{1e} is independent of the same. The physical explanation of T_{1e} 's being independent of concentration in the fast exchange limit in both Heisenberg and chemical exchanges, is that all the hyperfine lines saturate equally because of rapid exchange of spins among themselves and the measured T_{1e} should thus be the intrinsic spin lattice relaxation. However, a careful analysis of these data (Cheng and Weissman 1976) shows some interesting discrepancies. Although they predict, from steady state solution of Bloch equations in the presence of chemical exchange, that T_{1e}^{eff} should first decrease with the increase of concentration of the diamagnetic molecule in the slow exchange regime and then revert to the intrinsic T_{1e} at the fast exchange regime and become independent of the concentration of the diamagnetic molecule, and conclude the same from their experimental findings, they have not reported any data indicating this inversion behaviour. Moreover, their results in the slow exchange regime show that in the limiting case where the concentration of TCNE goes to zero, the T_{1e} is approximately $3.3 \mu\text{sec}$. This value may be taken to be the intrinsic spin lattice relaxation time at -9.2°C . On the other hand, they publish T_{1e} 's at the fast exchange regime at different temperatures from which one finds that T_{1e} increases with the increase of temperature; and since according to this T_{1e} is $1.76 \mu\text{sec}$ at 30.9°C , it will certainly not be $3.3 \mu\text{sec}$ at -9°C .

Our measurements of T_{1e} by the saturation recovery technique have been carried out on naphthalene negative ion, instead of TCNE^- , since the investigations formed a part of our general investigation on the measurements of T_{1e} 's of aromatic anions by saturation recovery technique. It should be obvious at the end that far more investigations are necessary before a clearer picture emerges and it is imperative that we investigate TCNE^- also. We are currently involved in this effort.

2. Experimental

2.1 Pulsed ESR spectrometer

The instrument used for the saturation recovery studies (Das *et al* 1985) was a home-built spectrometer similar to the one described by Fessenden *et al* (1981). The observed power and the pump power level could be independently controlled. The separation of the free induction decay signal and the saturation recovery signal from the observed M_y component of the magnetisation has been achieved by performing two sets of experiments with the phase of the pump power being changed by π radian between the two sets as has been suggested by Percival and Hyde (1975).

2.2 CW ESR spectrometer

For linewidth and intensity measurements of the ESR spectra, we used a modified Varian V4500 100 kHz field modulated x-band spectrometer (Khakhar *et al* 1966).

2.3 Chemicals

Commercial naphthalene was used after vacuum sublimation. The solvent dimethoxyethane (DME) from Aldrich Chemical Co., Inc., was distilled from sodium and dehydrated by lithium aluminium hydride. It was then vacuum-distilled into a vessel containing a sodium mirror and anthracene. Deep green colour of anthracene dianion showed that the solvent was free from oxygen or any other paramagnetic impurity.

2.4 Sample preparation

The negative ion radical of naphthalene was prepared by the alkali metal reduction process. To make the dilution of the solution so prepared easier by vacuum distillation, we have found it convenient to use a modified form of sample tube as shown in figure 1. The tube and the vessel at F were calibrated and could hold about 5 ml of liquid. The vessel E is a large bulb of 10 ml capacity. D is a small bulb attached to a narrow tube where a small piece of sodium was kept. The whole apparatus was then connected to a vacuum line through the standard joint A, keeping the vessel F in liquid nitrogen, which contained a known amount of naphthalene. After evacuating to about 10^{-3} torr, the sodium in D was gently evaporated and allowed to form a mirror just below the constriction B. The side arm was then disconnected from the main tube by sealing it at the constriction C. Some amount of DME was then brought to the vessel F by keeping it in liquid nitrogen and distilling under vacuum from a DME storage vessel already connected to the vacuum line. The amount of solvent transferred could be estimated from the graduation on this arm. The solvent was then degassed 3 times by 'freeze, pump and thaw' technique and eventually disconnected from the vacuum line by sealing it at the constriction B. Reaction took place when the dissolved naphthalene was brought in contact with the sodium mirror. It was left overnight in that position for the reaction to reach equilibrium. The advantage of the large vessel may now become apparent. If we want to dilute the sample by a factor of 2, say, we transfer about half the bulk solution to this vessel and keep F in liquid nitrogen. Only the solvent will then distill from E to F. The large volume of E will prevent the radical from going accidentally to the other side, even if the solution 'bumps' while distilling. The diluted solution in F may be made homogeneous by shaking and the resulting solution may be

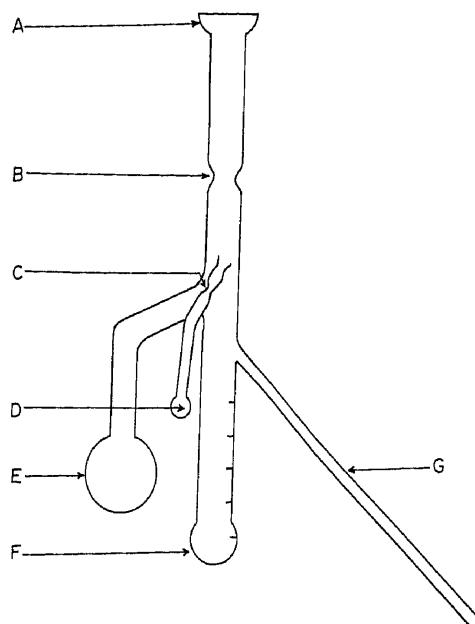


Figure 1. ESR sample tube: A—Standard joint; B, C—constrictions for sealing; D, E, F—storage bulbs; G—4 mm O.D. narrow tube for ESR measurement.

taken to the narrow tube G for ESR measurements. On the other hand, if we want to increase the concentration, we keep the vessel E in liquid nitrogen, so that only the solvent distils from F to E, and thus increases the concentration of the solution in F. The important point to be noted here is that, by this process we change the concentration of the radical as well as the neutral molecule maintaining their ratio constant.

Concentration of the naphthalene radical was estimated by comparing its signal intensity with that of a standard 1.1 mM 4-hydroxy-2,2,6,6-tetra-methyl-piperidinoxyl (TANOL) free radical recorded under similar conditions of the CW spectrometer. The formula used was (Poole 1967)

$$\frac{N^A}{N^B} = \frac{D^A}{D^B} \left\{ (\Delta H_{pp}^A)^2 (y_m^A / H_{mod}^A) \right\} / \left\{ (\Delta H_{pp}^B)^2 (y_m^B / H_{mod}^B) \right\}.$$

where N^i is the number of spins of the i th species whose degeneracy is D^i , first derivative peak-to-peak width ΔH_{pp}^i , peak-to-peak height Y_m^i for the field modulation amplitude H_{mod}^i . We determined the (Y_m^i / H_{mod}^i) factor by recording the first derivative spectra for different modulation amplitude. Lorentzian line shape was assumed for the TANOL and the naphthalene spectra that we have studied in the exchange narrowed region.

3. Results and discussion

A typical experiment consists of observing saturation recovery curves similar to those in figure 2 where the solid smooth line corresponds to a theoretical fit to an exponential.

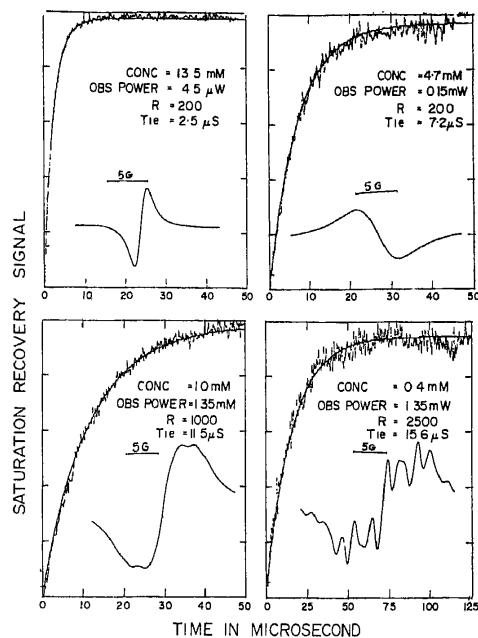


Figure 2. Saturation recovery curves for Na^+ naphthalene $^-$ in DME solution at 23°C for different dilutions. In each of them, the CW spectra are also depicted to indicate the change in line shapes with dilution. The noisy trace is the average signal of R experiments, while the smooth curves superimposed on them are fits to a single exponential with characteristic T_{1e} 's.

The different curves in figure 2 correspond to concentrations of the free radical varying from about 13 mM to 0.5 mM. It is observed that in all the cases the saturation recovery is exponential. Since the observed T_{1e} usually depends upon the level of microwave power used to observe the recovery from saturation it is customary to measure T_{1e} as a function of the observing microwave power and estimate the true T_{1e} from the limiting value at zero observing power, from a $1/T_1$ vs (observe power) $^{1/2}$ plot (Atkins *et al* 1973). However it was observed that T_{1e} was constant within error limit between 2.0 mW to 20 μ W of observing power for all the samples studied here. T_{1e} estimated in this manner was accurate to better than 10%. It may be noticed (figure 2) that the exponential nature of the recovery was followed from the slow exchange, where hyperfine structure was observed, to the fast exchange regime, where the hyperfine structure had been completely washed out resulting in a single narrow line.

Several samples with different initial concentration of naphthalene were investigated to determine the effect of Heisenberg exchange and the chemical exchange. The samples were diluted as described earlier keeping the ratio of $[\text{C}_{10}\text{H}_8^-]$ to $[\text{C}_{10}\text{H}_8]$ constant. In figure 3 the derivative peak-to-peak linewidths, ΔH_{pp} 's are plotted as a function of the naphthalene radical concentration for different samples with different amounts of unreacted naphthalene. It is indeed surprising that all the points fell on the same straight line, irrespective of the unreacted naphthalene concentration. All the points followed equation of the type

$$\Delta H = \Delta H_0 + \frac{A}{C} \quad (1)$$

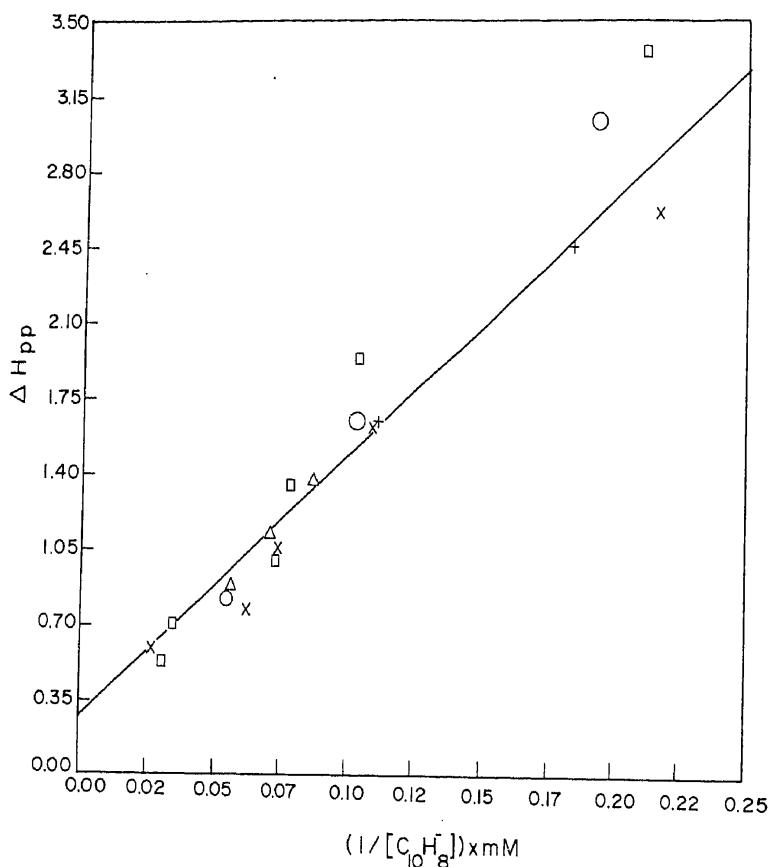


Figure 3. Plot of exchange narrowed peak-to-peak first derivative linewidths of Na^+ Naphthalene⁻ at 23°C as a function of reciprocal of the radical concentration for different samples differing in $[\text{C}_{10}\text{H}_8^-]$ to $[\text{C}_{10}\text{H}_8]$ in the equilibrium reaction mixture (see figure 4 for these concentrations). The ΔH_{pp} 's were measured in units of ΔH_{pp} of TANOL.

for the fast exchange regime (Molin *et al* 1980, p. 119). We had expected to find different curves for different initial concentration of naphthalene. However, it is to be noted that narrowing due to chemical exchange for this system is seen only at concentrations of naphthalene close to 100 mM (Ward and Weissman 1957). Apparently the narrowing observed in our case may be due to fast Heisenberg exchange which was manifested even at millimolar concentrations of the radical $\text{C}_{10}\text{H}_8^-$.

Dependence of T_{1e} on $[\text{C}_{10}\text{H}_8^-]$ is shown in figure 4. It appeared to follow an equation of the type

$$\frac{1}{T_{1e}} = \frac{1}{T_{1e}^0} + K_e C, \quad (2)$$

where $1/T_{1e}^0$ is the intrinsic spin lattice relaxation time, K_e the exchange rate constant and C the concentration of the radical. This equation is true only in the case of slow exchange of Heisenberg type (Molin *et al* 1980b, p. 521 eq 2-104). This figure shows that

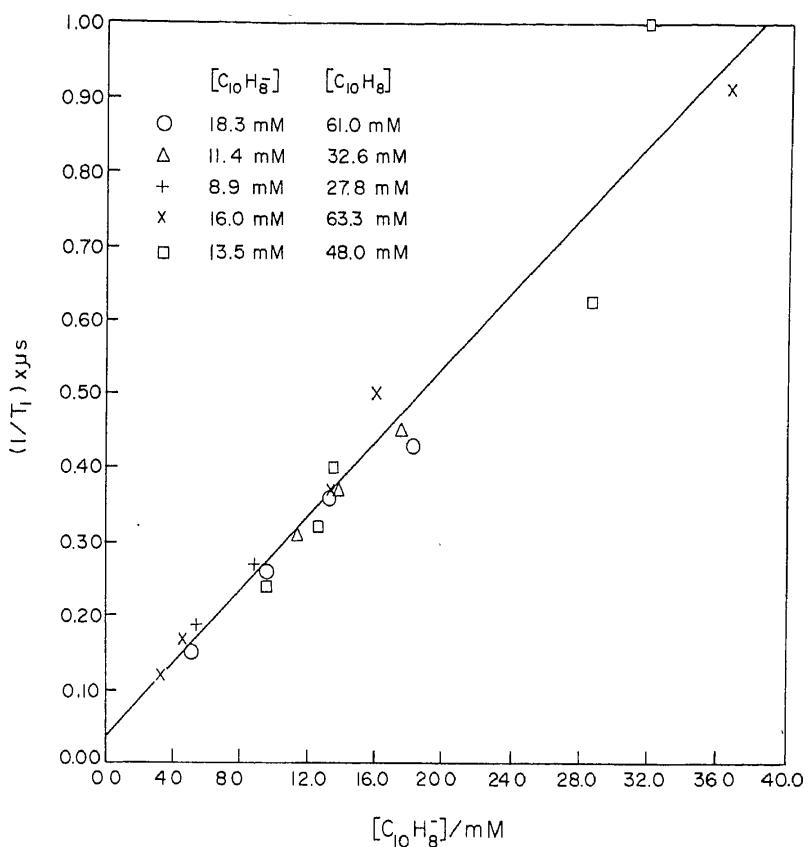


Figure 4. Dependence of $1/T_{1e}$ on $[C_{10}H_8^-]$ for different samples whose compositions of the equilibrium reaction mixtures are given at the top left corner.

the relaxation time T_{1e} was influenced mainly by the radical concentration and not by its diamagnetic precursor. It is further surprising that while earlier theory expects T_{1e} to be independent of the radical concentration in the fast exchange regime, we found T_{1e} to be dependent on it.

To further illustrate that the radical concentration $[C_{10}H_8^-]$ plays the dominant role in determining linewidth by Heisenberg exchange, we have measured the concentration and ESR linewidth as a function of time while allowing the naphthalene to react with the sodium mirror in the sample tube. Periodically the solution was removed from contact with the sodium mirror and measurement made (figure 5). We observed the narrowing of linewidth as the concentration of $C_{10}H_8^-$ increased with time. It should be emphasised that we always observed an unresolved broad line even at low radical concentration indicating that chemical exchange between $C_{10}H_8^-$ and $C_{10}H_8$ was present. It is, however, clear from this observation (figure 5) that Heisenberg exchange manifested itself at much lower radical concentration as compared to the concentrations required for effective chemical exchange.

In order to get a well-resolved spectrum, both $[C_{10}H_8^-]$ and $[C_{10}H_8]$ have to be low. In order to achieve this, the reaction mixture which had reached equilibrium after some

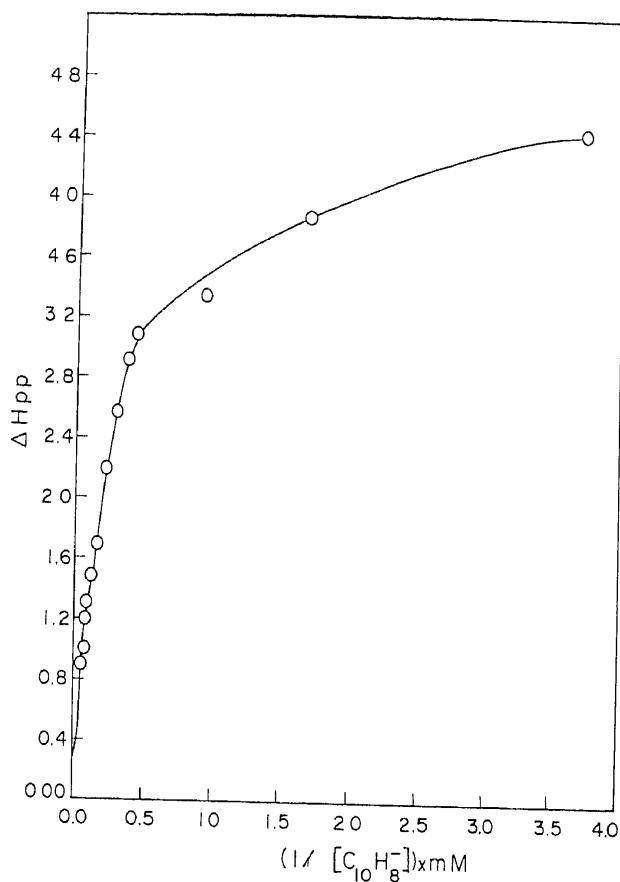


Figure 5. Dependence of peak-to-peak first derivative linewidth ΔH_{pp} as a function of naphthalene radical concentration during the progress of the reaction of naphthalene with sodium mirror. ΔH_{pp} 's were measured in units of ΔH_{pp} of TANOL.

time, had to be diluted adequately as described earlier thereby reducing both the concentrations. In such very dilute solutions, we were able to observe even the ^{23}Na hyperfine splittings in DME as solvent (figure 6) contrary to the finding of Atherton and Weissman (1961).

Mere applicability of equation (1) is not by itself an evidence of narrowing of lines brought about by bimolecular collision of particles causing exchanges of electron spins. For very concentrated solutions, exchange narrowing of ESR lines may occur as a result of the same mechanism as in the solid state where collisions of particles do not take place. It has been shown to be the case both by theory (Kivelson 1960) and by experiment (Molin *et al* 1980, p. 119) on aqueous solution of $\text{Cu}(\text{NH}_3)_5^{2+}$. This is termed as the static spin exchange for which the coefficient A in equation (1) does not depend upon temperature or viscosity of the solution. Thus in order to ascertain that our experiments were showing the exchange narrowing brought about by dynamic bimolecular collision, we proceeded as follows:

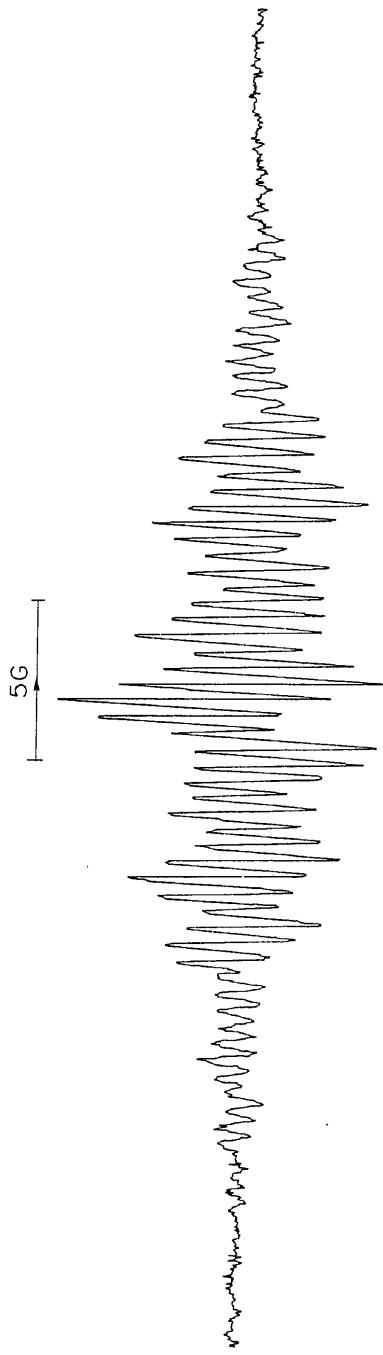


Figure 6. CW ESR spectrum of $\text{Na}^+ \text{C}_{10}\text{H}_8^-$ in DME at 23°C showing the hyperfine splittings of ^{23}Na .

The complete form of (1) for bimolecular collision is (Molin *et al* 1980, p. 117)

$$\Delta H = \Delta H_0 + 3.39 \times 10^6 \times g \sum_i I_i (I_i + 1) (\Delta H_{hf}^i)^2 / K_e C. \quad (3)$$

When g is the g -value of the radical with concentration C , ΔH_{hf}^i is the hyperfine coupling constant of the i th nucleus with nuclear spin I_i , K_e is the exchange rate constant. Keeping in mind that the rate constant follows the usual Arrhenius equation

$$K_e = a_0 \exp(-\Delta E/RT),$$

where a_0 is the pre-exponential factor, ΔE the activation energy, the other terms having the usual meaning, we may approximately write the temperature dependence of ΔH as

$$\Delta H = \Delta H_0 + \frac{A}{Ca_0} \exp(\Delta E/RT),$$

or

$$\ln(\Delta H - \Delta H_0) = \ln A - \ln a_0 - \ln C + \frac{\Delta E}{RT}. \quad (4)$$

Thus a plot of $\ln(\Delta H - \Delta H_0)$ should be linear in $1/T$ with a positive slope. Figure 7 shows such plots for three different samples. ΔH_0 for these plots was taken from the intercept of figure 3. The three plots are indeed linear and parallel to each other within experimental error. It may also be noted that the intercept follows the $-\ln C$ term of (4). This observation coupled with the one shown in figure 3, confirmed that we were

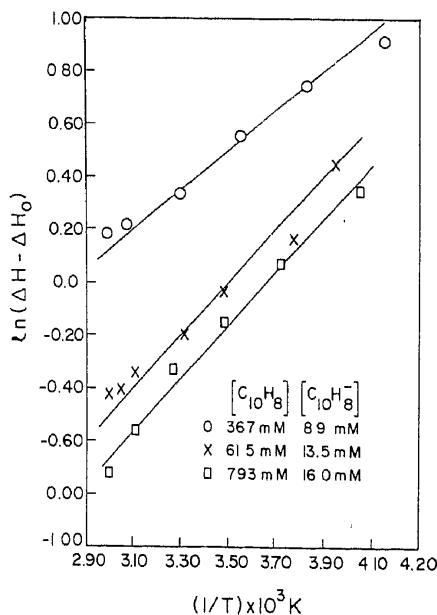


Figure 7. Plot of $\ln(\Delta H - \Delta H_0)$ of peak-to-peak derivative linewidth of naphthalene radical as a function of reciprocal of absolute temperature for three different samples—with different ratios of $[C_{10}H_8^-]$ to $[C_{10}H_8]$.

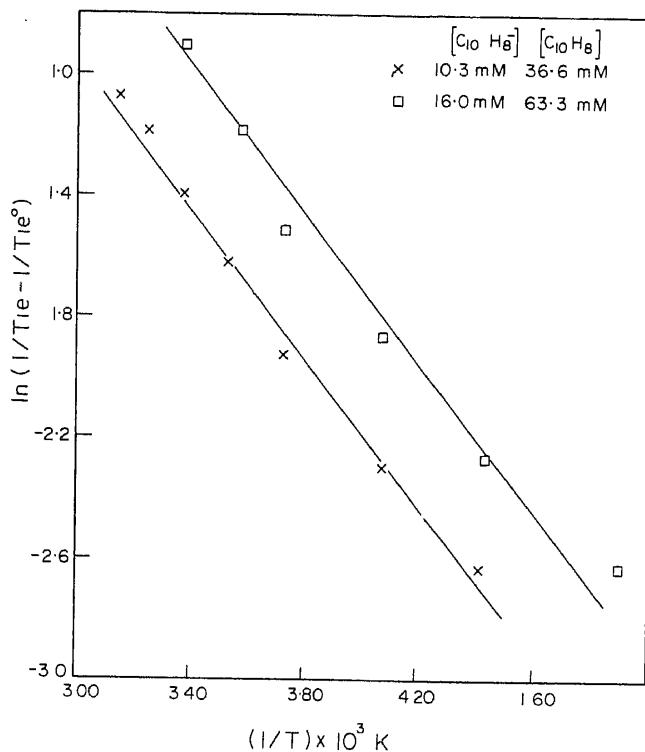


Figure 8. Plot of $\ln(1/T_{1e} - 1/T_{1e}^0)$ as a function of reciprocal of absolute temperature for two different samples with different ratios of $[C_{10}H_8^-]$ to $[C_{10}H_8]$.

observing phenomena brought about by binary collision of radicals in the fast exchange regime.

Applying the same arguments as above on (2) we could derive an approximate temperature dependence of T_{1e} . Applying the Arrhenius equation to the rate constant, we may write

$$\ln(1/T_{1e} - 1/T_{1e}^0) = \ln a_0 + \ln C - \frac{\Delta E}{RT}. \quad (5)$$

Figure 8 shows such plots of two different samples where T_{1e}^0 was taken from the intercept of figure 4. They are again parallel and the slope (1.2×10^3) has approximately the same magnitude as that obtained from figure 7 (0.9×10^3), but opposite in sign, giving an activation energy of 2.0 kcal/mol. Thus the mechanism responsible for narrowing of linewidth was also responsible for the change in the spin lattice relaxation times.

4. Conclusions

We have established that the Heisenberg spin exchange is more effective than chemical exchange at comparable concentrations for naphthalene anion radical and neutral

naphthalene system. Within the range of concentrations, we always found T_{1e} to be dependent upon the radical concentration even though it was firmly established that fast exchange was present in these concentration ranges. Earlier theory and experiment predict that T_{1e} should be independent of radical concentration in the fast exchange regime. In our case, however, it is necessary to differentiate between dipolar effects on T_{1e} from exchange effects before any conclusion can be arrived at. The processes that contribute to T_{1e} and linewidths in the fast exchange limit are similar since they showed the same temperature dependence with identical activation energy. A better understanding would emerge only when systems with simpler ESR spectrum (like TCNE⁻) are investigated by saturation recovery technique in the presence of chemical and/or Heisenberg exchange processes.

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