$$T^{2-}, 2Na^+ \rightleftharpoons T^{-}\cdot, Na^+, Na^0 \text{ (or } T^{-}\cdot, Na^+, e^-, Na^+)$$

is exceedingly fast.

The genuine expulsion of an electron from the T^{2-} ion into an adjacent solvent cage, or its capture by Na^+, should produce a $T\cdot^-$ radical ion, the formation of which could be recognized by its characteristic absorption band (λ_{max} = 660 nm). However, no absorption at 660 nm was detected in either system and the failure of observing the $T\cdot^-$ radical ion in THF may be accounted for in two ways. It has been suggested that $T\cdot^-$ and T^{2-} differ in geometry,[14] $T\cdot^-$ resembling T in its structure while T^{2-} acquires the shape of two connected $\bar{C}Ph_2$ planar groups placed in mutually perpendicular planes. Indeed, the 480-nm absorption band of the latter is identical with that of the $\bar{C}Ph_2$ chromophore in other compounds, e.g., $CH_3\text{-}\bar{C}Ph_2$. Accordingly, the excitation, even if accompanied by electron photoejection, could produce a distorted $T\cdot^-$ radical and its ground state would appear only after the $\bar{C}Ph_2$ groups had time to rotate, i.e., most likely after 60 psec, which is the long-time limit of the present experiments. No absorbance of the undistorted $T\cdot^-$ could be then observed.

The probability of autoionization of the excited T^{2-},$2Na^+$ is not too high even in THF. Our results indicate that more than half of the bleached species returned to their ground state in about 10 psec, while the return of the remaining ones was slow. The latter apparently represent the "distorted" $T\cdot^-$,Na^+ pairs, separated from the ejected electrons, which regenerate the dianions in a diffusion-controlled process. On this basis, we find the probability of electron ejection from T^{2-},$2Na^+$ in THF to be lower than 0.5.

It is interesting, therefore, to compare these results with those obtained in the photolysis of the salt of tetracene dianion, since in that system the electron photoejection is not followed by the rearrangement of the molecular framework. Flash photolysis of sodium salt of tetracene dianions in THF and in dioxane led to bleaching of the original absorption band and in both solvents the transient absorbance of the respective radical anion was recorded. It has been also established that the 530-nm picosecond pulse bleaches the absorbance band of potassium tetracene dianion ($\lambda_{max} \sim$ 630 nm) when its 2-MeTHF (2-methyltetrahydrofuran) or DME (dimethoxyethane) solutions are photolyzed; the transient corresponding to tetracene radical ion appears simultaneously with the bleaching. These results demonstrate that the probability of electron photoejection from tetracene dianion is much greater than from tetraphenylethylene dianion. They also suggest that the failure of detection of $T\cdot^-$ absorbance in the picosecond pulse photolysis of THF solution of T^{2-}, $2Na^+$ is most probably due to the substantially different shape of T^{2-} and $T\cdot^-$

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Flexibility of Molecular Chains Studied by Electron Spin Resonance Technique

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Received July 15, 1974

Abstract: A new experimental approach to dynamics of linear molecular chains has been developed. The method is illustrated by the following example. Hydrocarbons $N\text{-}(CH_2)_n\text{-}N$ (N denoting an α-naphthyl moiety) were reduced to $N\text{-}(CH_2)_n\text{-}N\cdot^-$ radical anions possessing only one extra electron per chain. ESR spectra of their highly dilute solutions in HMPA or in DME were recorded at a series of temperatures. Their shape is modified by the *intra*molecular electron transfer $N\text{-}(CH_2)_n\text{-}N\cdot^- \rightleftarrows {}^-\cdot N\text{-}(CH_2)_n\text{-}N$, and computer simulation of such spectra allows us to determine the frequency, P, of the transfer as a function of n and temperature. It has been found empirically that $P(n+1)^{3/2}$ is independent of n, provided that n is sufficiently large. The bimolecular rate constant, k_{ex}, of an analogous *inter*molecular electron transfer involving α-n-butylnaphthalene and its radical anions was determined in solvents and at temperatures chosen for the study of the *intra*molecular transfer. The merits of static and dynamic models of *intra*molecular reactions are discussed in light of our results.

Conformations of any molecular chain in a liquid medium are continually changed. Consider, for example, a molecule such as $X\cdot(CH_2)_n\cdot X$. Due to Brownian motion its end groups, X, perform random movements restricted only by the constrictions imposed by the chain binding them. In the course of this motion they approach each other and, if inert, they separate and after a time lag come together again. This motion continues ceaselessly and the frequency of such encounters is determined by the length of the chain, the nature of the end groups, temperature and viscosity of the sol-

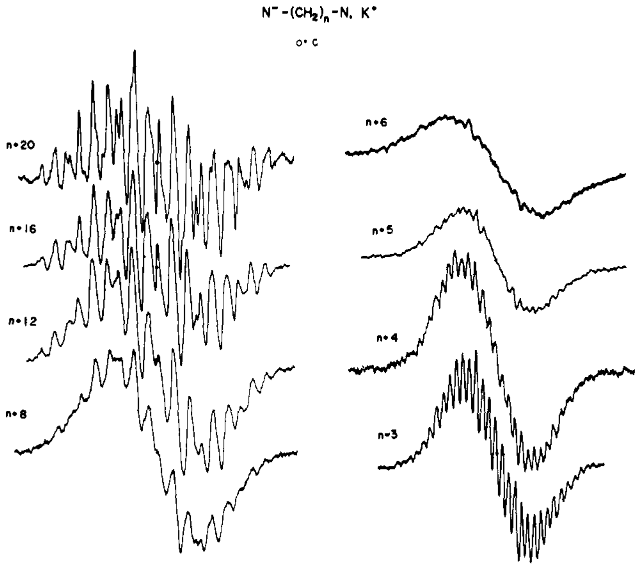


Figure 1. ESR spectra of $N-(CH_2)_n-N\cdot^-,K^+$ in HMPA for n = 20, 16, 12, 8, 6, 5, 4, and 3 at 0°.

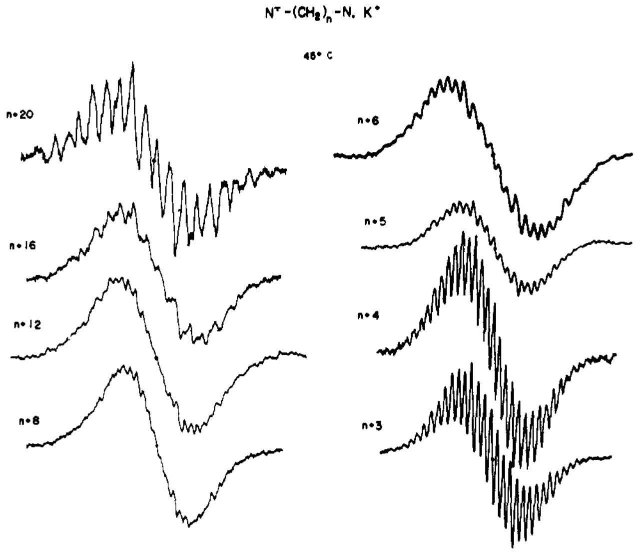


Figure 2. ESR spectra of $N-(CH_2)_n-N\cdot^-,K^+$ in HMPA for n = 20, 16, 12, 8, 6, 5, 4, and 3 at 45°.

vent, etc. Moreover, this frequency depends also on some intrinsic property of long, linear molecules that is *independent* of their length and which will be referred to as the *dynamic* flexibility of molecular chain. In this article we wish to discuss a method that might allow us to gauge the intrinsic dynamic flexibility of molecular chains and in the following one we shall consider some peculiarities observed in the behavior of short chains.

Our first approach to this problem was outlined elsewhere.[1,2] We prepared[3] for those studies a series of hydrocarbons $N-(CH_2)_n-N$, where N denotes an α-naphthyl moiety and n varied from 3 to 20. These hydrocarbons were partially reduced with potassium to afford HMPA (hexamethylphosphoric triamide) solutions of radical anions, $N-(CH_2)_n-N\cdot^-$, possessing *not more* than *one* electron per chain. Their ESR spectra were recorded at several temperatures, the dilution being sufficiently high ($[N-(CH_2)_n-N\cdot^-] < 10^{-4}$ *M*) to eliminate any effects arising from *inter*molecular reactions. For the sake of illustration, the ESR spectra of such radicals with n = 20, 16, 12, 8, 6, 5, 4, and 3, recorded at 0° and 45°, are shown in Figures 1 and 2.

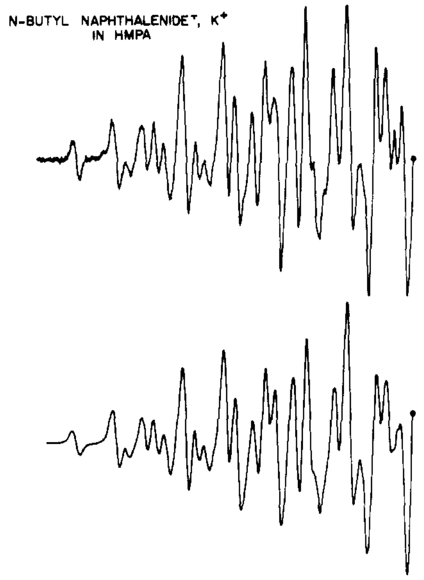


Figure 3. ESR spectrum of n-Bu-(α-N)$\cdot^-$,K$^+$ in HMPA. Upper: the observed spectrum. Lower: computer simulated spectrum using the coupling constants given in Table I.

Their shape appreciably changes with the length of the chain and is strongly affected by the temperature of solution.

The observed variations in the shape of the ESR spectra are caused by the *intra*molecular electron transfers

$$^{-}\cdot N-(CH_2)_n-N \rightleftarrows N-(CH_2)_nN\cdot^{-}$$

which occur whenever the end groups approach each other sufficiently close while being in orientations favoring the transfer. Therefore, the frequencies of such *intra*molecular "collisions" of the end groups may be deduced from the analysis of such spectra.

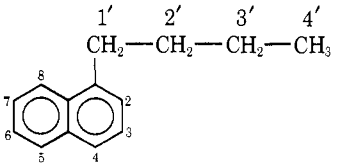
Calculation of Frequency of the Intramolecular Electron Transfer from the Shape of the ESR Spectrum

The ESR spectra of $N-(CH_2)_n-N\cdot^-$ should be virtually identical with those of radicals derived from appropriate mononaphthyl derivatives, e.g., n-butyl-α-naphthalene (n-BuN) or α-ethylnaphthalene (EtN), had it been possible to prevent the *intra*molecular "collisions" between their end groups. These collisions affect the spectra and alter their shape. At low rate of transfer the collisions broaden the hyperfine lines, while at high rate the spectra are gradually changed from those of monomers, $-CH_2N\cdot^-$, into these of hypothetic dimers $(-CH_2N)_2\cdot^-$.

The observed spectra of $N-(CH_2)_n-N\cdot^-$ may be computer simulated had one known the coupling constants of the odd electron with the seven aromatic and two α-methylenic protons. It is plausible to assume that these coupling constants are the same for $N-(CH_2)_n-N\cdot^-$ and, say, for n-$BuN\cdot^-$. We analyzed therefore the spectrum of the latter radical, shown in Figure 3, and summarized the results in Table I.

The ESR spectra of $N-(CH_2)_n-N\cdot^-$ radicals were then computer simulated by a method outlined by Harriman and Maki.[4] The solution was treated as if it were a mixture of various kinds of radicals, each kind having a fixed configuration of proton spins. In each radical the odd electron oscillates between two magnetic environments, it resonates at frequency ω_A when located on one naphthyl group but at frequency ω_B when associated with the other. The resonance frequencies ω_A and ω_B are any two of those corre-

Table I. Coupling Constants of *n*-Butyl-α-naphthalenide[a]



Proton	*a* in THF, G, at 10°	*a* in HMPA, G, at 25°	*a* in DME,[b] G
2	1.60	1.53	
3	1.77	1.68	
4	4.10	4.46	
5	5.20	5.09	
6	1.65	1.62	
7	2.03	2.02	
8	5.10	4.89	
1′	2.58	2.78	2.80
2′	0.155	0.130	−0.155
3′	0.045[b]	0.045[b]	0.045
4′	0.035[b]	0.035[b]	0.035

[a] The assignments are based on the analogy with the *a* constants reported for α-Me-naphthalenide·⁻ (R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, **51**, 1765 (1969)) and α-Et-naphthalenide·⁻ (G. Moshuk, H. D. Connor, and M. Szwarc, *J. Phys. Chem.*, 76, 1734 (1972)). [b] E. de Boer and C. MacLeen, *Mol. Phys.*, 7, 191 (1965). The coupling constants for 3′ and 4′ protons were assumed to be the same in THF and HMPA as those reported by de Boer for DME.

sponding to the 384 lines of the $-CH_2N\cdot^-$ radical, and the mixture is composed of about 70,000 kinds of species, each representing one of the $(\omega_A;\omega_B)$ pairs.

The ESR spectrum of each kind of radicals is calculated with the aid of Gutowsky's equation.[5] Their complex magnetization, **M**, is deduced from a modified Bloch equation

$$\mathbf{M} = \frac{\omega - \bar{\omega} + (i/T_2) + 2iP}{(\omega - \omega_A + (i/T_2))(\omega - \omega_B + (i/T_2)) + 2iP(\omega - \bar{\omega} + (i/T_2))},$$

where $\bar{\omega} = \frac{1}{2}(\omega_A + \omega_B)$, $1/T_2$ gives the width of the individual Lorentzian lines in the absence of exchange broadening, and P is the frequency of electron jumps between the two environments. The imaginary part of **M** gives the intensity of the absorption at frequency ω for a $(\omega_A;\omega_B)$ pair, and the summation for all the 70,000 pairs gives the ESR absorption spectrum of $N-(CH_2)_n-N\cdot^-$ radical in which the electron oscillates with frequency P between the two end groups. The differentiation of the absorption spectrum yields the conventional spectrum as recorded by the ESR spectrometer. Examples of computed spectra are shown in Figure 4, and the details of matching with the experimental ones are given in ref 6.

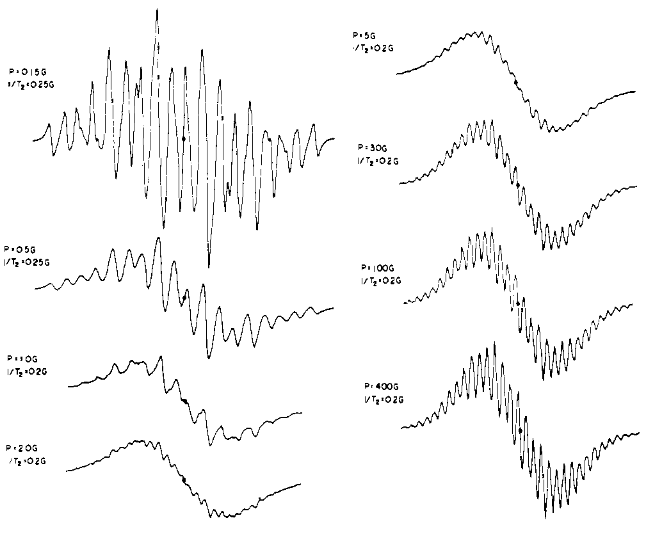


Figure 4. Computer simulated ESR spectra of $N-(CH_2)_n-N\cdot^-$ for P values varying from 0.15 to 400 G.

Determination of T_2

The previously mentioned 384 lines are in fact multiplets, each arising from further splitting caused by the protons of the second CH_2 (a = 0.13 G), the third (a = 0.045 G), and the fourth (a = 0.035 G). These multiplets were computer simulated; their shape is Lorentzian and the width ($1/T_2$ = 0.2 G) is independent of P, provided that P is in the range of 1 to 500 G and the width of the input line greater than 0.02 G. (It is customary to give the values of the frequency P and of $1/T_2$ in gauss (G). A factor 1.76×10^7 is applied to convert gauss into the conventional sec^{-1} unit used in kinetics.) For $P < 1$ G one finds $1/T_2$ = 0.25 G. These $1/T_2$ values were used in generating the computer simulated spectra.

How Far Can Electron Be Transferred?

The concept of "collision" between two naphthyl moieties measured by our ESR technique calls for estimation of the distance across which electron is transferred before the naphthyl groups are parted. With this aim in mind we prepared a cyclohexane having the equatorial hydrogens on carbon atoms 1 and 4 substituted by $-CH_2N$ groups.[7] Inspection of its molecular model demonstrates that the two α-naphthyl substituents can never be closer than about 8 Å apart. Reduction to the radical anion, $NCH_2-C_6H_{10}-CH_2N\cdot^-$, and examination of its ESR spectrum revealed that the rate of *intra*molecular electron transfer in hexamethylphosphoric triamide is about 10^7 sec^{-1} at ambient

$$NCH_2-C_6H_{10}-CH_2N\cdot^- \rightleftarrows {}^-\cdot NCH_2-C_6H_{10}-CH_2N$$

temperature.[7] We conclude, therefore, that a "collision" between two α-naphthyl groups measured by electron transfer may occur on their approach to about 7–9 Å, i.e., the collision cross section of these reactions is large and no closed ring need be formed in this process.

Some General Comments

Electron transfer, like any "bimolecular" solution reaction, involves three steps: meeting of the reacting molecules (or groups), the actual reaction, and the separation of the products. In an exchange discussed here this scheme involves three rate constants as illustrated by a truly bimolecular reaction

$$X\cdot^- + X \underset{k_s}{\overset{k_d}{\rightleftarrows}} (X\cdot^-, X) \underset{k_t}{\overset{k_t}{\rightleftarrows}} (X, X\cdot^-) \underset{k_d}{\overset{k_s}{\rightleftarrows}} X + X\cdot^-$$

and leads to the observed bimolecular rate constant, k_{ex}, given by

$$k_{ex} = k_d k_t/(2k_t + k_s)$$

For a slow reaction, i.e., for $k_t \ll k_s$, this expression is reduced to

$$k_{ex} = (k_d/k_s)k_t = Kk_t$$

where the constant K represents the equilibrium constant of properly oriented encounter complexes. In the other ex-

Table II. Rate Constants for Electron Transfer in HMPA, n-Bu-α-N$\cdot^-$ + n-Bu-α-N $\rightleftharpoons$ n-Bu-α-N + n-Bu-α-N$\cdot^-$, for Spin–Spin Exchange and HMPA Viscosity[d]

T, °C	k(electron transfer), M^{-1} sec^{-1} [a,c]	k(spin exchange), M^{-1} sec^{-1} [a,b]	η(cP)/HMPA
−15	2.0×10^8	2.3×10^8	
0	3.0×10^8	3.4×10^8	6.23
15	4.9×10^8	5.0×10^8	4.24
30	7.1×10^8	7.3×10^8	3.03
45	9.8×10^8	10.7×10^8	2.22
60			1.71

[a] The rate constants were determined from the concentration dependence of the width of the end line of the ESR spectra. The values for the line width were corrected for the effects due to overlap with the next line. [b] The spin-exchange studies were performed by varying the radical concentration from 2.6×10^{-3} to 16.1×10^{-3} M. [c] [n-BuN$\cdot^-$] = 8×10^{-4} M. [d] E(electron transfer) = 4.3 kcal mol^{-1}. E(spin exchange) = 4.0 kcal mol^{-1}. $-E$(viscosity) = 3.9 kcal mol^{-1}. These data have been recalculated. They differ slightly from those published earlier.[2]

treme, when $k_t \gg k_s$, the reaction becomes diffusion controlled, i.e., $k_{ex} = \frac{1}{2}k_d$.

Table III. Comparison of *Inter*molecular Electron Exchanges in HMPA[a]

System	n-Bu-α-N	α-EtN	β-EtN
E, kcal/mol	4.3	4.2	4.1
A, M^{-1} sec^{-1}	7.8×10^{11}	8.3×10^{11}	5.9×10^{11}
k_{30}, M^{-1} sec^{-1}	7.1×10^8	7.0×10^8	6.9×10^8

[a] n-Bu-α-N = n-butyl-α-naphthalene; α-EtN = α-ethylnaphthalene; β-EtN = β-ethylnaphthalene.

Viscosity of solvent usually affects k_d and k_s to the same degree, and hence in reactions in which $k_t \ll k_s$ the observed rate constant, k_{ex}, is virtually unaffected by changes of the medium's viscosity.

The same considerations apply to *intra*molecular reaction like that discussed in this work. For a very slow exchange the measured frequency P is determined by $\Sigma K_i f_i$ where K_i represents the conformational equilibrium constant of a mutual orientation of the interacting groups at which the electron is transferred f_i times per second. In the extreme of very rapid transfer the rate of conformational changes becomes the limiting term.

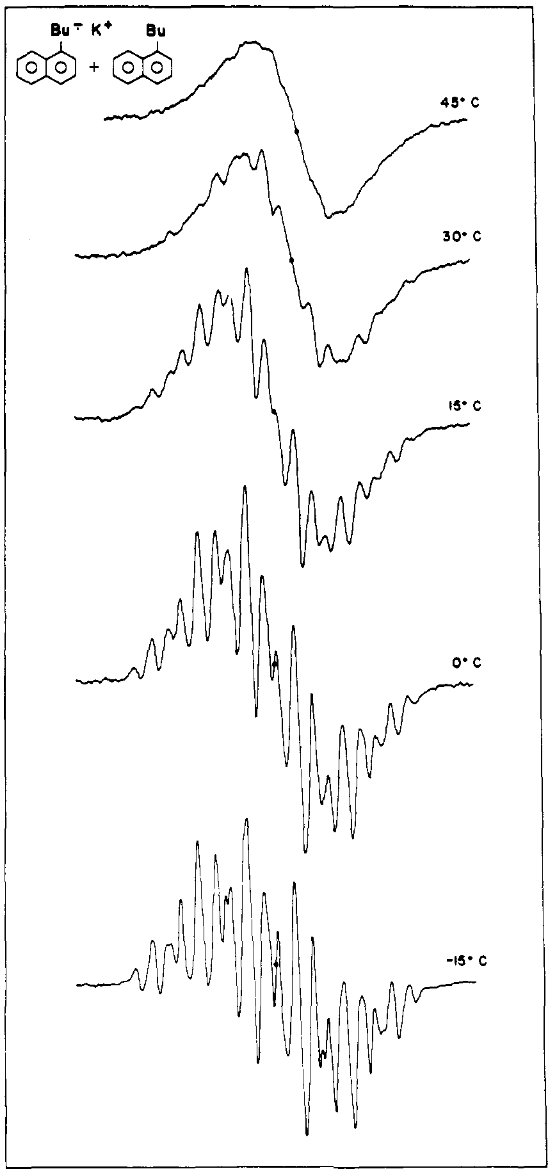


Figure 5. ESR spectra of n-Bu-(α-N)$\cdot^-$ in 2.5×10^{-2} M solution of n-Bu-(α-N) in HMPA at temperatures ranging from −15 to +45°.

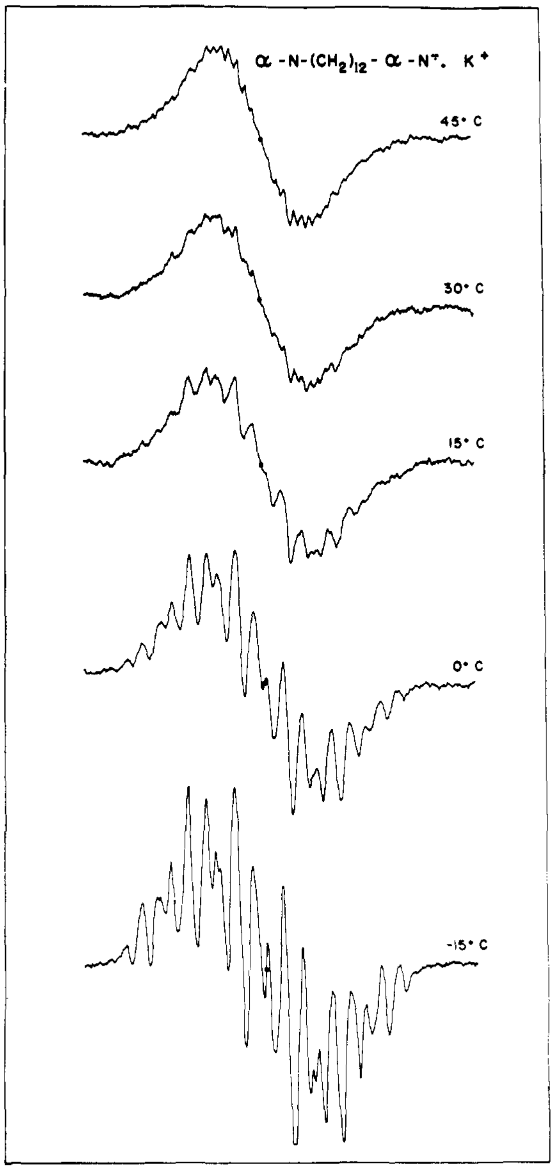


Figure 6. ESR spectra of N-(CH$_2$)$_{12}$-N$\cdot^-$ in HMPA at T = −15, 0, 15, 30, and 45°.

Comparison of the Intra- and Intermolecular Electron Transfer

Electron exchange is relatively inefficient when the donor forms ion pairs[8,9] but the reaction becomes nearly diffusion controlled for free ionic donors.[9-11] We have chosen initially HMPA as the solvent to ensure that virtually all the radical ions are present as free ions[12] since then the exchange is nearly diffusion controlled.

The remarks in the preceding section stress the need for studying bimolecular electron transfers such as

$$n\text{-BuN}^{\cdot -} + n\text{-BuN} \rightleftarrows n\text{-BuN} + n\text{-BuN}^{\cdot -}$$

This has been done,[1,2] and the bimolecular rate constants, k_{ex}, of the *inter*molecular transfer proceeding in HMPA are given in Table II. They were derived from the extent of broadening of the first ESR line, seen in the spectrum depicted in Figure 3, caused by the addition of *n*-BuN. The degree of broadening was corrected for any overlap between the first and the second ESR lines. The concentration of *n*-BuN in these experiments varied from 1×10^{-3} to 1×10^{-2} *M;* for the concentrations lower than 10^{-3} *M* the broadening was imperceptible. This last point justifies our previous statement, namely, that the contribution of *inter*molecular transfer was negligible in the experiments performed with $\text{N-(CH}_2)_n\text{-N}^{\cdot -}$ radical anions.

The bimolecular exchange in HMPA proceeds with activation energy of 4.3 ± 1.0 kcal mol^{-1} and $A = 7.8 \times 10^{11}$ M^{-1} sec^{-1}. The relatively high activation energy reflects the high activation energy of the diffusion process. The temperature dependence of the viscosity of HMPA was measured (the pertinent data are included in Table II) and the linear plot of log η vs. $1/T$ led to activation energy of 3.9 kcal mol^{-1}.

To ascertain the reliability of our data, we investigated also the electron exchange between α- or β-ethylnaphthalenide and the respective parent hydrocarbon. The pertinent results are collected in Table III and show that the rate of the transfer is nearly the same for all these naphthalenides. We studied also the rate of the spin-spin exchange, a reaction which is essentially diffusion controlled, the results being included in Table II. These rates are virtually identical with those of the electron transfer.

Alternative Method for Determining Frequency *P* of Intramolecular Electron Transfer

The bimolecular electron transfer may serve as a reference for the *intra*molecular transfer. This approach is clarified by inspection of Figure 5 giving the ESR spectra of *n*-Bu-α-$\text{N}^{\cdot -}$ radical anions in HMPA in the presence of the parent hydrocarbon kept at a concentration of 2.5×10^{-2} *M*. This concentration of the acceptor was chosen through trial and error experiments, the intention being to match the ESR spectrum of a bimolecular system at −15° with that of the $\text{N-(CH}_2)_{12}\text{-N}^{\cdot -}$ recorded at the same temperature, the latter being shown in Figure 6. Inspection of both figures shows that both spectra are indeed identical implying that at −15° the rate of *inter*molecular transfer at the concentration of the acceptor of 2.5×10^{-2} *M* is the same as the rate of *intra*molecular transfer for $n = 12$. Knowing the bimolecular rate constant of the former and the concentration of the acceptor, we calculate the rate of the bimolecular reaction and therefore the frequency of the *intra*molecular electron transfer. In the same way the frequency of *intra*molecular rate transfer may be found for other relatively slowly exchanging systems.

Can we compare the ESR spectra obtained in the systems in which the exchange takes place through *intra*molecular reaction with those involving *inter*molecular exchange? In

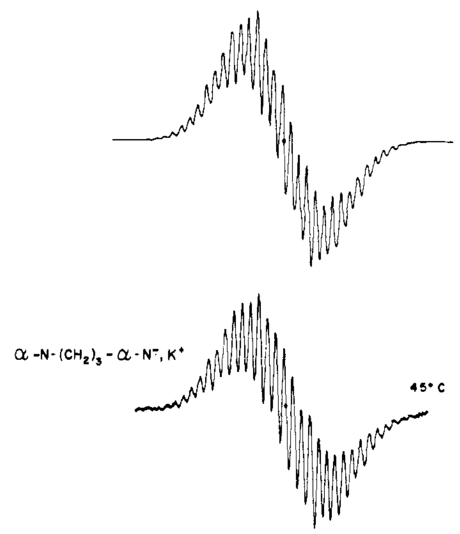


Figure 7. Computer simulated ESR spectrum of the hypothetic dimer $(\text{—CH}_2\text{N})_2{}^{\cdot -}$ and the spectrum of $\text{N-(CH}_2)_3\text{-N}^{\cdot -}$ recorded at 45°.

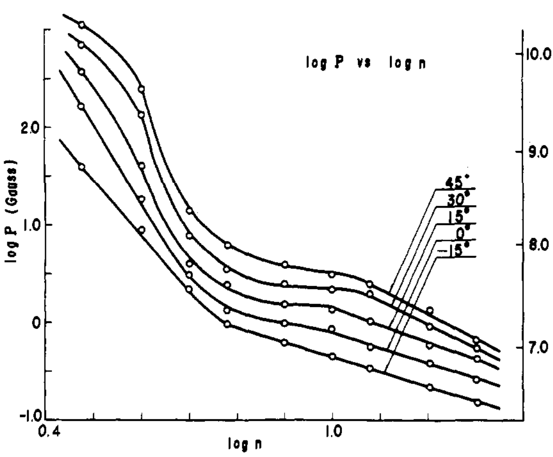


Figure 8. Log *P* as a function of log *n* for constant temperatures, −15, 0, 15, 30, and 45°. Solvent HMPA.

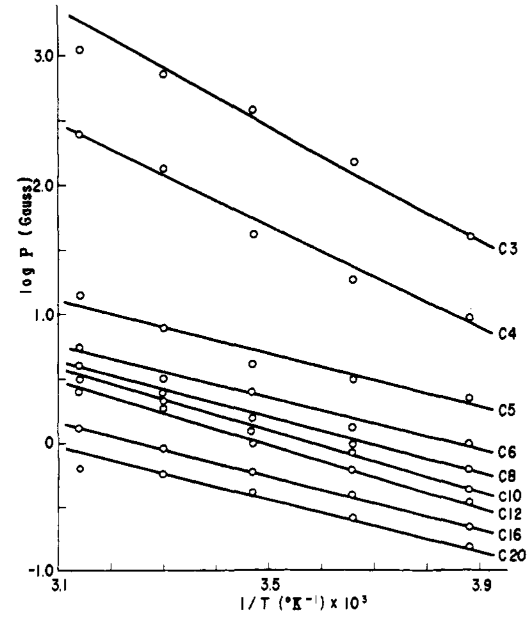


Figure 9. Arrhenius plots of log *P* vs. $1/T$ for constant *n*'s. Solvent HMPA. $E = 5.0 \pm 0.4$ kcal/mol for $n > 5$, but for $n = 3$, $E = 10.5$ kcal/mol and for $n = 4$, $E = 8.9$ kcal/mol.

Table IV. Frequencies of *Intra*molecular Electron Exchange, P, in $N-(CH_2)_n-N\cdot^-$ in HMPA (unit sec^{-1})

n	−15°	0°	15°	30°	45°
3	7.0×10^8	2.6×10^9	6.7×10^9	1.3×10^{10}	1.9×10^{10}
4	1.6×10^8	3.3×10^8	7.2×10^8	2.5×10^9	4.4×10^9
5	3.9×10^7	5.6×10^7	7.2×10^7	1.4×10^8	2.5×10^8
6	1.8×10^7	2.3×10^7	4.4×10^7	6.3×10^7	1.1×10^8
8	1.1×10^7	1.8×10^7	2.8×10^7	4.3×10^7	6.9×10^7
10	8.1×10^6	1.6×10^7	2.3×10^7	3.9×10^7	5.6×10^7
12	6.6×10^6	1.1×10^7	1.8×10^7	3.5×10^7	4.4×10^7
16	3.9×10^6	7.0×10^6	1.1×10^7	1.6×10^7	2.3×10^7
20	2.6×10^6	5.5×10^6	7.4×10^6	1.0×10^7	1.1×10^7

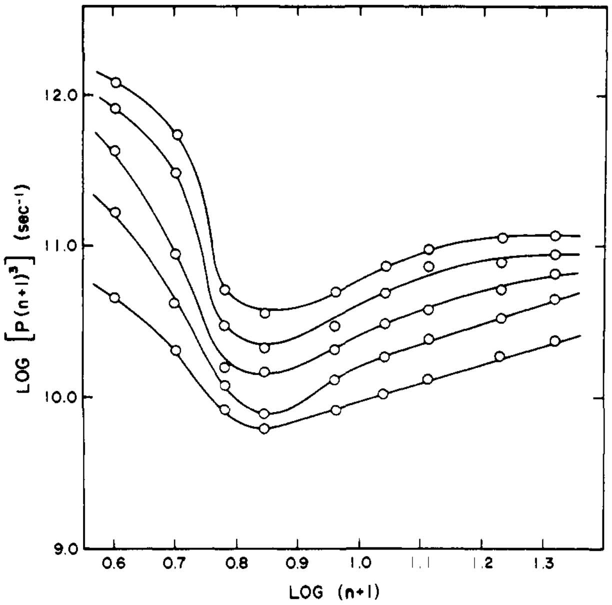


Figure 10. Log $\{P(n + 1)^3\}$ as a function of log $(n + 1)$ for constant temperatures. From the bottom up, $T = -15, 0, +15, 30$, and 45°. Solvent HMPA.

the *intra*molecularly exchanging system an electron is transferred backwards and forwards between two naphthyl moieties having different but fixed proton spin configurations, say configurations a and b. In the *inter*molecularly exchanging system an electron is transferred, say from a naphthyl moiety having the proton spin configuration a to that having the configuration b, but thereafter it moves to another naphthyl moiety having the configuration c, and so on. However, what ESR spectrometer records is not reflecting the fate of a single electron but the behavior of the whole sample. In the *intra*molecularly exchanging system all the possible pairs of α-naphthyl moieties are present, and therefore all the possible electron transfers are observed. Statistics of these systems are the same as those of the *inter*molecularly exchanging sample, and therefore the matching is permitted provided that the electrons remain for a sufficiently long time on naphthyl moieties before they are transferred.

In the intermediate and fast exchange regions, the latter method fails. [Atherton has pointed out in a recent note (*Chem. Phys. Lett.*, **23**, 454, 1973) that the *intra-* and *inter*molecular electron transfer affects in a different way the ESR spectra of the exchanging species. Nevertheless, as remarked by him, the differences of shape are negligible in the slow exchange and they become even less pronounced when the number of different protons is large. In fact, we carried out the computer simulation for the ESR spectrum of $N-(CH_2)_n-N\cdot^-$ radical anions using the programs for the *intra*molecular and for the *inter*molecular exchange and found identical results when $p < 1$ G.] The ESR spectrum of the *inter*molecularly exchanging system collapses then into one featureless line (see the upper spectrum in Figure 5) which sharpens as the exchange becomes faster. In contrast, the ESR spectrum of the *intra*molecularly exchanging system approaches in the fast exchange limit that of a hypothetic dimer $(-CH_2\cdot N)_2\cdot^-$. The spectrum of the latter species was computer simulated; its coupling constants are ½ of those of $—CH_2N\cdot^-$ but the number of protons is doubled. For the sake of illustration, the computed spectrum of the hypothetic dimer is shown in Figure 7 together with the experimental spectrum of $N-(CH_2)_3-N\cdot^-$ recorded at 45°, the latter referring to the fastest observed rate of *intra*molecular exchange. The agreement between both spectra is excellent.

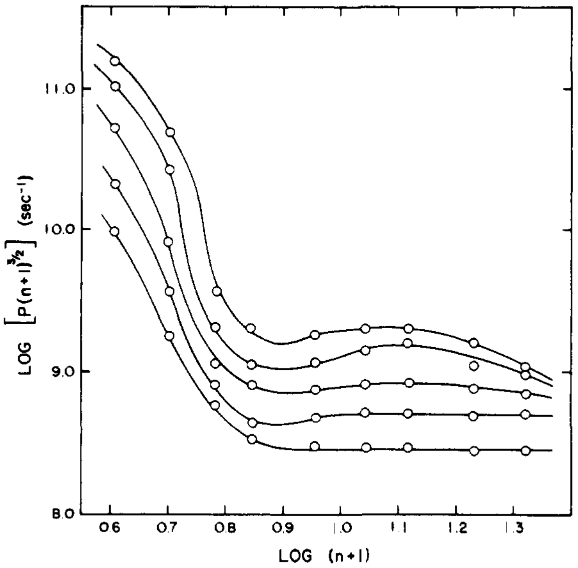


Figure 11. Log $\{P(n + 1)^{3/2}\}$ as a function of log $(n + 1)$ for constant temperatures. From the bottom up, $T = -15, 0, +15, 30$, and 45°. Solvent HMPA.

Let us point out that the alternative method, whenever applicable, gives the same values of P as the general one.

The Results Obtained in HMPA Solution

The results of the above investigations are summarized in Table IV. The dependence of log P on log n is given by Figure 8 for a series of constant temperatures, while the Arrhenius plots of log P vs. $1/T$ for constant n's are shown in Figure 9. Inspection of Figure 8 shows that P is a monotonic function of n that sharply decreases as n increases from 3 to 4 and 5. The striking differences in the "activation energies" of the systems corresponding to different n's are clearly revealed by Figure 9. The activation energy is exceptionally high when $n = 3$, slightly lower when $n = 4$, and still lower, but virtually constant, for the remaining systems ($n \geq 5$).

Significance of the Results

The *intra*molecular exchange exhibits a feature resembling a bimolecular reaction. The acceptor, -N, attached to one end of a chain can never be further away from the donor, $-N\cdot^-$, which is attached to the other end, than the length of the extended chain. We may treat, therefore, the *intra*molecular exchange as if it were a "bimolecular" electron transfer in a system where one molecule of a donor and another of an acceptor are enclosed in a sphere of appropriate volume, the latter being determined by the length of the chain. Such a system becomes more "dilute" as the length

Table V. The Effective Concentrations, C_{eff}, of the Acceptor –N in the *Intra*molecular Electron Transfer, $N-(CH_2)_n-N\cdot^- \rightleftharpoons {}^-\cdot N-(CH_2)_n-N$ Proceeding in HMPA ($C_{eff} = P/k_{ex}$, units M/l.)

n	T, deg C –15	0	+15	+30	+45	C_{min}[a]
8	0.055	0.060	0.057	0.061	0.071	0.284
10	0.040	0.053	0.047	0.055	0.057	0.155
12	0.033	0.037	0.037	0.050	0.045	0.094
16	0.020	0.023	0.022	0.022	0.024	0.042
20	0.013	0.018	0.015	0.014	0.011	0.022

[a] C_{min} is the minimum concentration of the acceptor calculated as 1 molecule in a sphere of radius equal to the length of the *extended* chain.

Table VI. The Bimolecular Rate Constants, k_{ex}, for Electron Transfer Bu-N·$^-$, K$^+$ + Bu-N → Exchange in DME (+2% HMPA)[a]

T, deg C	$k_{ex} \times 10^{-8}$, M^{-1} sec^{-1}	Viscosity, cP
–75	0.56	
–60	0.88	1.69
–45	1.5	
–30	2.3	0.93
–15	3.2	
0	4.2	0.61
+15	6.0	

[a] E_{ex} = 3.0 kcal/mol, $A_{ex} = 1.0 \times 10^{11}\ M^{-1}$ sec^{-1}, $-E_\eta$ = 1.95 kcal/mol.

of the chain increases, and this dilution contributes to the decrease of P caused by an increase of n.

The trivial dilution factor should be excluded from our consideration when a deeper significance of P is contemplated. In the most naive treatment, the radius of the hypothetic sphere is assumed to be proportional to the length of the extended chain, i.e., proportional to the number, $n + 1$, of bonds separating the naphthyl moieties. The experimental P values could therefore be normalized by multiplying them by $(n + 1)^3$. The plots of log $\{P(n + 1)^3\}$ vs. log $(n + 1)$, graphed for a series of increasing temperatures, are shown in Figure 10. The resulting curves reveal an intriguing minima for $n = 6$, but for $n \geq 6$ log $\{P(n + 1)^3\}$ continually rises and no approach to a plateau is seen for larger values of n. However, intuitively one feels that the properly normalized P should become constant for large n's, and hence the above normalization procedure seems to be inappropriate for this system.

We found empirically that P may be normalized if multiplied by $(n + 1)^{3/2}$, i.e., the radius of the hypothetic sphere seems to be proportional to $(n + 1)^{1/2}$. The plots of log $\{P(n + 1)^{3/2}\}$ vs. log $(n + 1)$ are shown in Figure 11. The minima seen in Figure 10 disappear and the resulting curves seem to approach their asymptotic values, at least at the lower temperature range, although the curves drawn for $T = 30$ and 45° show shallow maxima. It is uncertain whether these maxima are real or whether they reflect some experimental errors. Tentatively, we accept the latter alternative and consider the average value of $P(n + 1)^{3/2}$ obtained for $n \geq 6$ at each of the constant temperatures as a characteristic constant providing a measure of the intrinsic chain flexibility. Although these constants are independent of n, they still depend on temperature of the solution, viscosity of the solvent, and the character of the end groups, as well as on the nature of the chain.

Dynamic or Static Model of Intramolecular Exchange?

The frequency P of *intra*molecular exchange may be treated as a rate of *inter*molecular electron transfer occurring at appropriate concentration of the acceptor. Assuming that the frequency of transfer between two interacting groups having a particular mutual orientation is the same whether the reaction is *inter-* or *intra*molecular, we find this effective concentration of the acceptor to be given by the ratio P/k_{ex}. Thus calculated values of $C_{eff} = P/k_{ex}$ are listed in Table V. However, the acceptor -N can never be further away from the donor -N·$^-$ than the length of the *fully extended* chain, i.e., its *minimum* "concentration" in moles per liter is given by $3000/4\pi l^3 N$, where l denotes the length of the fully extended chain and N is the Avogadro number. These minimum concentrations, given for each chain in the last column of Table V, are substantially larger, by a factor of 2–5, than C_{eff}.

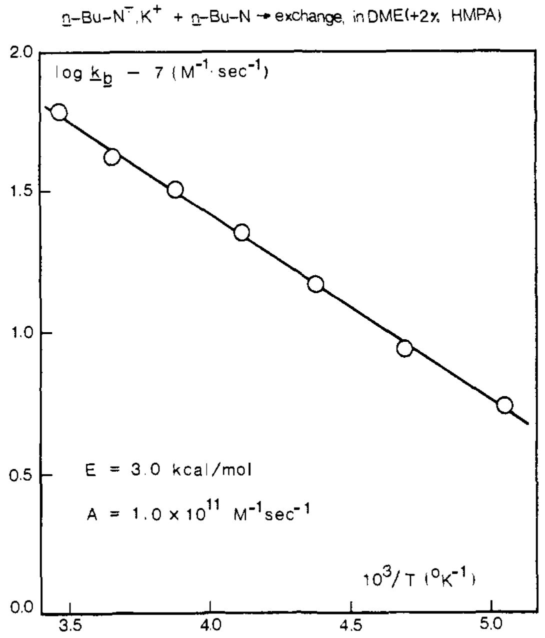


Figure 12. Arrhenius plot of log k_{ex} vs. $1/T$. k_{ex} is the bimolecular rate constant of exchange, n-Bu-N·$^-$,K$^+$ + n-Bu-N → exchange, in DME (+2% HMPA). E = 3.0 kcal/mol. $A = 1.0 \times 10^{11}\ M^{-1}$ sec^{-1}.

A static model of *intra*molecular reaction assumes that the *equilibrium* distribution of mutual configurations of the interacting groups determines its rate. Denoting by K_i the configurational equilibrium constant of each orientation of the interacting groups and by f_i the frequency of electron exchange between them when locked in this orientation, one finds the observed frequency of the *intra*molecular electron transfer to be $P = \Sigma K_i{\cdot}f_i$. Of course, K_i depends on the length and nature of the chain linking the interacting groups.

It is highly unlikely that such a model would yield values of P substantially smaller than $k_{ex}{\cdot}C_{min}$ for n's being in the range of 8–20. This would demand the fraction of favorable configurations permitting the exchange to be smaller for $N-(CH_2)_n-N\cdot^-$ than for a freely moving -N moiety enclosed in a sphere having radius of a fully extended chain while -N·$^-$ is located in its center. It seems therefore that the chain retards the motion of the interacting groups and this effect is reflected in the values of P. The factor $(n + 1)^{3/2}$ accounts for the changes in C_{eff}, at least within the range of n studied by us, and hence $P(n + 1)^{3/2}$ gives a measure of dynamic flexibility of a chain.

The Effect of Solvent's Viscosity

To obtain information about the effect of solvent's viscosity we investigated the kinetics of the previously studied

Table VII. *Intra*molecular Electron Exchange Rate of $N-(CH_2)_n-N^{\cdot -}$ in DME (+2% HMPA)[a]

	Temperature, deg C						
n	−75	−60	−45	−30	−15	0	+15
3	6.3×10^7	2.4×10^8	3.1×10^8	4.0×10^8	4.7×10^8	4.6×10^8	4.4×10^8
4	5.1×10^6	1.3×10^7	5.6×10^7	1.1×10^8	2.8×10^8	3.1×10^8	3.9×10^8
5	2.5×10^6	5.2×10^6	8.8×10^7	1.6×10^7	2.5×10^7	3.5×10^7	5.0×10^7
6	1.9×10^6	3.5×10^6	6.9×10^6	1.2×10^7	2.0×10^7	2.5×10^7	3.3×10^7
8	1.3×10^6	2.2×10^6	3.6×10^6	7.2×10^6	1.1×10^7	1.3×10^7	1.7×10^7
10	1.2×10^6	1.6×10^6	3.3×10^6	5.0×10^6	9.8×10^6	1.1×10^7	1.5×10^7
12	8.8×10^5	1.4×10^6	2.4×10^6	3.6×10^6	6.7×10^6	8.8×10^6	1.3×10^7
16	5.7×10^5	8.1×10^5	1.8×10^6	2.9×10^6	4.5×10^6	5.6×10^6	7.0×10^6
20	3.9×10^5	6.4×10^5	1.3×10^6	2.2×10^6	3.4×10^6	4.2×10^6	5.2×10^6

[a] Unit sec^{-1}.

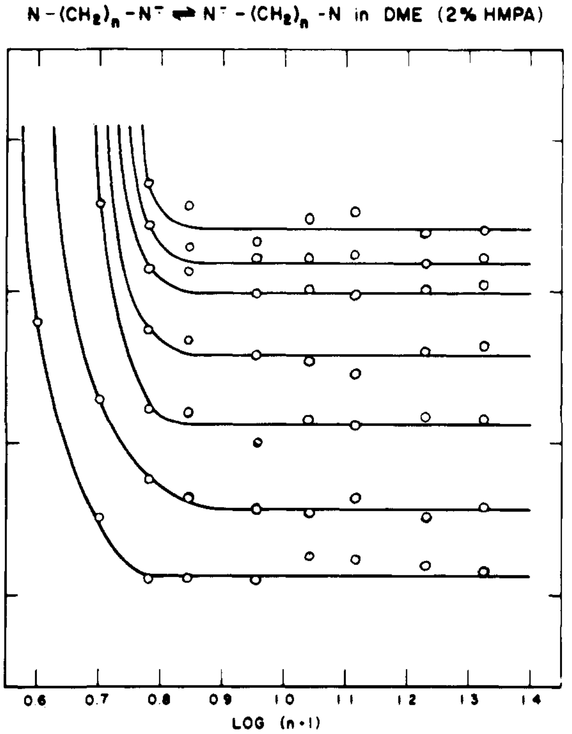


Figure 13. Log $\{P(n+1)^{3/2}\}$ as a function of log $(n+1)$ at constant temperatures (−75, −60, −45, −30, −15, 0, and +15°). Solvent DME (+2% HMPA).

inter- and *intra*molecular electron transfers proceeding in dimethoxyethane (DME) containing 2% of hexamethylphosphoric triamide (HMPA). This study covered a wider temperature range, viz., from −75 to +15°. The bimolecular rate constants are given in Table VI and the respective Arrhenius line is shown in Figure 12. The activation energy is higher than the medium viscosity (see Table VI), but the k_{ex}'s determined at 0 or 15° are slightly greater than the respective k_{ex}'s in HMPA. The rates of intramolecular process, P, are listed in Table VII and graphically displayed in Figure 13 as plots of log $\{P(n+1)^{3/2}\}$ vs. log $(n+1)$ at a series of constant temperatures. Such plots reached plateau values for $n > 6$, this being their most significant feature.

Comparison of P or $P(n+1)^{3/2}$ determined at 0 and 15° in both solvent systems shows that they virtually are identical, although the viscosities of these media are greatly different. This could be taken as a further evidence favoring the dynamic model of this *intra*molecular reaction in which the resistance of the chain, and not the viscosity of the solvent, determines the motion of the interacting groups. Unfortunately, bimolecular rate constants are also similar in both solvents and this casts doubt on the above conclusion. We hope to clarify these problems in the course of further work.

Concluding Remarks

The dynamic flexibility of a chain should be distinguished from its static flexibility. The latter determines those properties of a chain that depend on the multitude of its conformational states *but not on time,* e.g., its average end-to-end distance or the probability of ring closure between two designated points on its chain, etc. In contrast, the dynamic flexibility is a measure of the *rate* of conformational changes, which could be reflected in the frequency of the *intra*molecular collisions between the end groups of a linear polymer provided the studied reaction is sufficiently fast. Of course, the probability of ring closure is an important factor determining the frequency of "tight" collisions but not the only one. It is possible to visualize two polymeric molecules of the same length, one being more flexibile than the other in the static meaning of that term, but less flexible if the dynamic criterion of flexibility is used in the comparison.

Electron transfer process was chosen as a tool. However, it is not our intention to examine here the intricate details of this process. It suffices to say that the investigated reaction occurs during encounters of the two end groups and is not mediated by the chain, a possibility discussed by other investigators.[4,13,14]

Finally, we should draw the reader's attention to a similar study by Goodman and Morawetz[15] who investigated the catalytic effect of pyridyl group attached to one comonomer on the hydrolysis of *p*-nitrophenyl ester group attached to another comonomer. The results were treated in terms of "effective" concentrations, a concept similar to that applied in our work. However, the reaction studied by them is slow and therefore the static model accounts for the results. The need of considering the distribution of the reactive groups along the chain greatly complicates the treatment of their results. Goodman and Morawetz conclude that the excluded volume effect is important. The importance of the excluded volume in our study has to await further results.

Acknowledgment. It is a pleasure to acknowledge the financial support of these studies by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation. We wish to thank Professor Stig Claesson for drawing our attention to the problem of *intra*molecular collisions and we also thank Dr. M. A. Winnik for his constructive comments. After completion of this paper we learned about the most interesting theoretical study of Wilemski and Fixman[16] concerned with diffusion-controlled interchain reaction. We shall discuss their work in our future publication.

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The Peculiarities of Intramolecular Electron Transfer in α-Naphthyl-$(CH_2)_3$-α-naphthyl$\cdot^-$ and α-Naphthyl-$(CH_2)_4$-α-naphthyl$\cdot^-$ Radical Anions

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Received July 19, 1974

Abstract: *Intra*molecular electron transfer in α-naphthyl-$(CH_2)_3$-α-naphthyl$\cdot^-$ and α-naphthyl-$(CH_2)_4$-α-naphthyl$\cdot^-$ radical anions was investigated. For $n = 3$ or 4, the reaction described by the equation $N\text{-}(CH_2)_n\text{-}N\cdot^- \rightleftarrows {}^-\cdot\dot{N}\text{-}(CH_2)_n\text{-}N$ shows peculiarities not observed in those involving the analogous compounds having $n > 5$ (5, 6, 8, 10, 12, 16, and 20). These peculiarities are reported, discussed, and tentatively accounted for. The electron transfer occurs at long distance, whereas the formation of *intra*molecular charge-transfer complexes, excimers, or exciplexes requires a close approach of the interacting groups. This accounts for the different behavior of these two types of systems.

Using the method described in the preceding article, we determined[1] the frequency of *intra*molecular electron transfer between two naphthyl moieties linked by a chain of n CH_2 groups, i.e.,

$$N\text{-}(CH_2)_n\text{-}N\cdot^- \rightleftarrows {}^-\cdot N\text{-}(CH_2)_n\text{-}N$$

We investigated such hydrocarbons with chains containing 3 to 20 CH_2 groups and have shown that for those corresponding to $n \geq 5$ the frequency of transfer, P, varies inversely with $(n + 1)^{3/2}$, the proportionality constant being determined by temperature and solvent. The "activation energy" of P was found to be independent of n, provided that $n \geq 5$, namely, its value is about 5.0 ± 0.4 kcal/mol for the reactions proceeding in HMPA and ~3 kcal/mol when the transfer takes place in DME (+2% HMPA). However, these simple relations fail when $n = 3$ or 4. For those short chains the frequency P is much higher than predicted by the equation discussed above, and, strangely enough, the respective activation energies are also substantially higher, namely, in HMPA $E = 10.5$ kcal/mol for $n = 3$ and 8.9 kcal/mol for $n = 4$.

The above *intra*molecular electron-transfer reactions may be treated as if they were bimolecular exchanges between a single donor and a single acceptor when enclosed in a sphere of radius R with a length proportional to $(n + 1)^{1/2}$. However, the crowding severely restricts the motion of the naphthyl groups when $n = 3$ or 4, and this may increase the potential energy barrier associated with the conformational changes leading from the orientations unfavorable for the exchange to those that permit the electron transfer. Furthermore, as the naphthyl moieties acquire the configurations allowing the exchange they become squeezed too closely together. For example, in $N\text{-}(CH_2)_3\text{-}N\cdot^-$ they are separated only by ~2.5 Å when in juxtaposition, the orientation seemingly the most favorable for the electron transfer. At this distance the repulsion forces should be appreciable, and the need to overcome them could be partially responsible for the high activation energy of the exchange observed in this system. (This distance is slightly shorter than that separating the naphthalene molecules in a crystal (~3 Å) or in a charge-transfer complex (3.5-4 Å). The presence of an additional electron on one of the naphthyl units is expected to increase even more the repulsion at such a close approach.) In addition, some HMPA molecules which were oriented by the field of the $-N\cdot^-$ ion have to be squeezed out when $-N$ approaches so closely the $-N\cdot^-$ group. This desolvation further augments the activation energy of the transfer, and contributes to the high A factor of the exchange in the $N\text{-}(CH_2)_3\text{-}N\cdot^-$ system ($\sim 3 \times 10^{17}$ sec^{-1}), because it increases the entropy of the transition state.

A similar situation is encountered in the electron-transfer process taking place in the $N\text{-}(CH_2)_4\text{-}N\cdot^-$ system. However, the steric strain is then weaker and the desolvation of the $-N\cdot^-$ ions is less extensive than in the $N\text{-}(CH_2)_3\text{-}N\cdot^-$ system.

Two problems should be considered before the behavior of the $N\text{-}(CH_2)_3\text{-}N\cdot^-$ and $N\text{-}(CH_2)_4\text{-}N\cdot^-$ systems could be comprehended. (1) At what distance does the electron transfer from an $-N\cdot^-$ donor to an $-N$ acceptor occur with a reasonable rate? (2) How close may an $-N$ group approach an $-N\cdot^-$ radical anion before encountering the repulsion?

Our recent studies of electron transfer[2] in 1,4-$N\text{-}CH_2\text{-}c\text{-}C_6H_{10}\text{-}CH_2\text{-}N\cdot^-$ demonstrate that the frequency of the *intra*molecular transfer between the naphthyl units is still