References and Notes

(1) M. Szwarc, *Proc. Nobel Symp., 22nd, ESR* [*Electron Spin Reson.*] *Appl. Polym. Res.*, 291 (1973).
(2) H. D. Connor, K. Shimada, and M. Szwarc, *Macromolecules*, **5**, 801 (1972).
(3) P. Caluwe, K. Shimada, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 1433 (1973).
(4) J. E. Harriman and A.H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).
(5) See, e.g., A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, N.Y., 1967, p 207.
(6) K. Shimada, Ph.D. Thesis, Syracuse, N.Y., 1973.
(7) K. Shimada and M. Szwarc, *Chem. Phys. Lett.*, **28**, 540 (1974).
(8) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957).
(9) S. I. Weissman, *Z. Elektrochem.*, **64**, 47 (1960).
(10) N. Hirota, R. Carraway, and W. Schook, *J. Am. Chem. Soc.*, **90**, 3611 (1968).
(11) K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **91**, 4645 (1969).
(12) A. Cserhegyi, E. Franta, J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 7129 (1967).
(13) H. M. McConnell, *J. Chem. Phys.*, **35**, 508 (1961).
(14) F. Gerson and J. M. Martin, *J. Am. Chem. Soc.*, **91**, 1883 (1969).
(15) N. Goodman and H. Morawetz, *J. Polym. Sci., Polym. Phys. Ed.*, **9**, 1657 (1971).
(16) G. Wilemski and M. Fixman, *J. Chem. Phys.*, **60**, 866, 878 (1974).

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.,

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

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 $\text{-}N\cdot^-$ ion have to be squeezed out when -N approaches so closely the $\text{-}N\cdot^-$ 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 $\text{-}N\cdot^-$ 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 $\text{-}N\cdot^-$ donor to an -N acceptor occur with a reasonable rate? (2) How close may an -N group approach an $\text{-}N\cdot^-$ radical anion before encountering the repulsion?

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

Table I. The Frequency of Electron Transfer, P, for $N{-}(CH_2)_n{-}N\cdot^-$ at 15°

n	P in HMPA, sec^{-1}	P in DME (+2% HMPA), sec^{-1}
20	7.4×10^6	5.2×10^6
16	1.1×10^7	7.0×10^6
12	1.8×10^7	1.3×10^7
10	2.3×10^7	1.5×10^7
8	2.8×10^7	1.7×10^7
6	4.4×10^7	3.3×10^7
5	7.2×10^7	5.0×10^7
4	7.2×10^8	3.9×10^8
3	6.7×10^9	4.4×10^8

about 10^7 sec^{-1} although they are separated by 9 Å. Recent findings of Weller and his associates[3] support our observation. Their studies of fluorescence quenching in acetonitrile showed that this process involves an electron transfer from the quencher, Q, to the excited molecule, A*, which takes place when the partners are 7 Å apart. Subsequently, an $A\cdot^- \cdots Q\cdot^+$ pair separated by this distance, and not the exciplex, is the primary product of quenching. In conclusion, the *intra*molecular electron exchange between the two naphthyl moieties linked by a long chain ($n \geq 5$) occurs when the interacting groups are separated by two or three solvent molecules; a direct contact between them is unnecessary. The same spacial conditions apply in the *inter*molecular exchange. However, as we pointed out earlier, the problem is different for n = 3 or 4. In these molecules the exchange has to take place when the interacting naphthyl moieties are placed too closely together, a conformation associated with the high repulsion energy but often encountered because the short chain forces the naphthyl groups to remain always in the vicinity of each other.

The radicals $N{-}(CH_2)_n{-}N\cdot^-$ having $n \geq 5$ are, most of the time, in conformations unfavorable for electron transfer. On the average, they attain the favorable conformations $\bar{f}$ times per second and retain them for a relatively short time, τ, i.e., $\tau \ll 1/\bar{f}$. The average frequency of electron transfer when the radical acquires the favorable conformation is denoted by p and is assumed to be temperature independent. In most systems the product $p\tau$ seems to be large, i.e., $p\tau \gg 1$, and therefore there is ½ probability that an electron residing on one of the two -N groups before the encounter finds itself on the other as the -N groups separate. Hence, the frequency, P, that affects the shape of the observed ESR spectrum is independent of p and equals $(1/2)\bar{f}$, and since $\bar{f}$ increases with temperature, so does p.

The temperature dependence of P for the $N{-}(CH_2)_3{-}N\cdot^-$ system, and to a lesser extent also for the $N{-}(CH_2)_4{-}N\cdot^-$ system, is greatly affected by the repulsion experienced by the reacting N moieties when they are squeezed together too closely, and by the energy of partial desolvation of the $-N\cdot^-$ ions. Nevertheless, the value of P is high due to two factors mentioned previously: the crowding, i.e., the high "concentration" of the N groups, and because the partial desolvation of $-N\cdot^-$ increases the entropy of the transition state.

The exchange in DME (+2% HMPA) is slower than in HMPA, in spite of the much lower viscosity of the former solvent than of the latter. (For example, at 15° the viscosity of HMPA is η = 4.24 cP but only 0.5 cP for DME (+2% HMPA).) The two oppositely charged ions are paired in DME, but not in HMPA, and the necessity of transferring the cation hinders the electron transfer. This hindrance is affecting the *intra*molecular reaction as well as the *inter*molecular transfer.

The cation transfer affects in a specific way the *intra*molecular exchange in $N{-}(CH_2)_3{-}N\cdot^-$ and $N{-}(CH_2)_4{-}N\cdot^-$. In the transition state of the reaction the cation has to be placed between the interacting naphthyl moieties. However, in the short-chain radicals this may be only achieved when the planes of the naphthyl moieties are inclined to each other, i.e., when the conformation of the radical is not too favorable for the exchange. Consequently, the exchange is relatively slow. For example, at 15° the ratio P (for n = 3)/P (for n = 5) is about 100 in HMPA but only 10 in DME (see Table I).

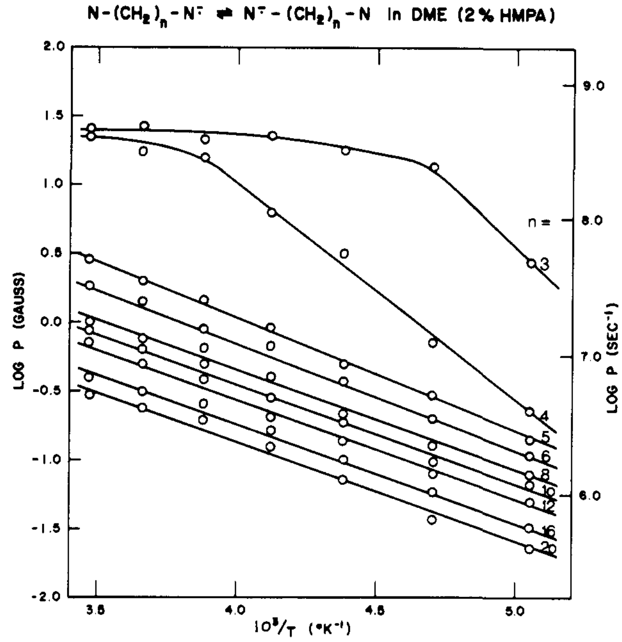


Figure 1. Arrhenius plot of the frequency P of *intra*molecular electron exchange in $N{-}(CH_2)_n{-}N\cdot^-$ in DME (2% HMPA).

A most interesting peculiarity of the $N{-}(CH_2)_3{-}N\cdot^-$ system is revealed by Figure 1. It shows that P becomes temperature independent at higher temperatures when the exchange occurs in DME but not in HMPA, a phenomenon observed also, although within a narrower temperature range, in the $N{-}(CH_2)_4{-}N\cdot^-$ system. The following explanation may account for these observations.

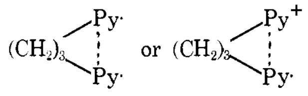
As suggested previously, in most of the investigated systems $p\tau \gg 1$. However, since p is low for the paired radicals present in DME, and, for the reasons stated above, even lower for $N{-}(CH_2)_3{-}N\cdot^-$, it is plausible to expect $p\tau \ll 1$ for $N{-}(CH_2)_3{-}N\cdot^-$ in DME, especially at higher temperatures when τ is short. Under such conditions, $P = \bar{f}\tau p$ and not $\frac{1}{2}\bar{f}$. Now, $\bar{f}$ and τ depend on temperature; as it rises the former increases while the latter decreases and therefore their product is expected to be only slightly temperature dependent. Thus, since p is assumed to be temperature independent, P becomes virtually constant.

An alternative explanation for the independence of P on temperature should be considered. Hirota's studies of bimolecular electron transfer[4] showed that the reactive loose pairs, abundant at low temperature, are converted into the unreactive tight pairs as the temperature rises. This conversion counteracts the conventional effect of rising temperature and could be responsible for the observed effect. However, this explanation is not acceptable since it demands the temperature independence of P not only for the $N{-}(CH_2)_3{-}N\cdot^-$ system but also for those with $n \geq 5$ as well as for bimolecular exchange. Our results (see, e.g., Figure 1) contradict this prediction.

There is a basic difference between the behavior of our system and the processes leading to *intra*molecular formation of charge-transfer complexes, excimers, or exciplexes.

For example, an *intra*molecular association leading to the formation of charge-transfer complexes was described by Itoh and Kosower.[5] They studied the dipyridyl diradicals, $\cdot$Py-$(CH_2)_n$-Py$\cdot$ (-Py$\cdot$ = -p-$C_5H_4\dot{N}COOCH_3$, $n = 3$, 4, or 5), in a mixture of isopentane and 3-methylpentane. Determination of spin concentration by ESR technique led to the conclusion that only 2% of the radicals are free and not *intra*molecularly associated when $n = 3$, their fraction increases to 20% for $n = 4$, and no association is observed for $n = 5$. Interestingly, no cyclomers are formed when $n = 2$, provided the solution is sufficiently dilute to prevent an *inter*molecular association.[6] Spectroscopic evidence[7] suggests that the diamagnetic "cyclomers" are charge-transfer complexes having the pyridyl groups oriented parallel to each other. We can conclude, therefore, that this *intra*molecular dimerization requires relatively close approach of the interacting groups favored when $n = 3$.

Itoh[8] extended these studies to radical cations $\cdot$Py-$(CH_2)_n$-Py^+. Again, the closed form is abundant for $n = 3$ but hardly detected, if at all, for $n = 5$. An interesting point transpires from these results. The half-width of the absorption band attributed to the closed form is larger for the diradical $\cdot$Py-$(CH_2)_3$-Py$\cdot$ (~6000 cm^{-1}) and the radical cation (~3800 cm^{-1}) than for the dimers formed from the monomeric radicals (~1800 cm^{-1}). This implies a difference in the structure of



A B

on one hand and that of an *inter*molecularly formed $(Py\cdot)_2$ or $(Py\cdot^+Py)$ on the other. The equilibrium distance between the Py moieties of the *inter*molecular dimers is apparently greater than 2.5 Å and such a species resides in a relatively steep potential energy well. In the *intra*molecular A "cyclomer" the closeness of the Py moieties, when in juxtaposition, squeezes the interacting groups too close to each other, and hence this *intra*molecular associate resides in a relatively flat potential energy well. This factor, as well as the unfavorable conformation of the chain, may account for the difference in the half-width of the absorption band of the *inter*molecular dimer and of A. The ΔH of such *intra*molecular dimerization (−5.6 kcal/mol) was determined from the studies of similar heterodiradicals.[9] It is unfortunate, however, that the ΔH of the *inter*molecular dimerization is not available.

Formation of excimers furnishes additional information on the ease of ring closure by association of aromatic end groups. Hirayama[10] studied the formation of excimers of α,ω-diphenylalkanes, Ph-$(CH_2)_n$-Ph, with n varying from 1 to 6. He concluded that excimers are formed only for $n = 3$ and the following rational was proposed to account for this observation. (1) Benzene rings of an excimer have to be parallel to each other. (2) They should not be further apart than about 3.5 Å. (3) The -$(CH_2)_n$- chain must attain the low energy, staggered conformation. Requirement 1 rules out the possibility of an excimer formation for $n = 1$ and 2, while the combined requirements 2 and 3 rule out the formation of excimers for $n = 4$, 5, or 6.

The geometry of excimers was discussed by several workers. Most of the theoreticians[11-14] favor a sandwich structure with the interplanar distance somewhat smaller than that in graphite (~3.5 Å), although Birks[15] argued that some displacement (by ~1.4 Å) along one of the molecular axes may be advantageous, because it would reduce the repulsion between the interacting groups The experimental approach to the problem of geometry of excimers was developed by Chandross and Dempster.[16] These workers studied the formation of intramolecular excimers in α,α-, β,β-, and α,β-dinaphthyl-1,3-propane, 1,2-di-α-naphthylethane, and 1,4-di-α-naphthylbutane. The first two hydrocarbons may attain a parallel sandwich configuration, but in the third, α,β, the molecular axes are inclined to each other by ~45° when the aromatic planes are parallel.

Solutions of these hydrocarbons in methylcyclohexane-isopentane mixture were irradiated at sufficiently low temperature range to render the dissociation of the excimer negligible. In the absence of quenching, the ratio of fluorescence intensities of the excimer and the excited naphthyl is proportional to k_a/k_{fD}, where k_a is the unimolecular rate constant of the *intra*molecular excimer formation and k_{fD} is the rate constant of its fluorescence. The temperature dependence of k_a/k_{fD} gives therefore the activation energy, E_a, of the excimer formation. For the α,α- and β,β-1,3-dinaphthylpropanes E_a is 3.3 and 4.0 kcal/mol, respectively. Since the actual process of the *inter*molecular excimer formation is diffusion controlled,[17] E_a (of the *intra*molecular process) is affected only by solvent's viscosity and by the chain stiffness. The results obtained for α,β-1,3-dinaphthylpropane indicate a much lower binding energy of the complex, inplying that the twisting of molecular axes decreases the stability of the excimer, contrary to the suggestion of Birks.[15] Finally, the fluorescence of the excimer formed from 1,4-dinaphthylbutane is very weak; hence the unfavorable conformation of the connecting chain hinders its formation, an observation confirming the findings of Hirayama.[10] The advantageous position of the C_3 chain in the formation of excimers is again confirmed by the work of Leonard and his associates[18] who studied the formation of the photodimer of 1,3-bisthyminepropane.

This brief review shows that the formation of charge-transfer complexes or excimers requires a close approach of interacting aromatic moieties, but even for the dimers bonded in this way the repulsion becomes notable at separations less than 3 Å. Such a close approach is not needed for the electron transfer and, in fact, when the constraints due to the shortness of chain force the close approach of the interacting groups, the system exhibits then the peculiarities discussed in this article.

Acknowledgment. We gratefully acknowledge the National Science Foundation and The Petroleum Research Fund, administered by the American Chemical Society, for the financial support of this study.

References and Notes

(1) (a) K. Shimada and M. Szwarc, preceding paper in this issue; (b) H. D. Connor, K. Shimada, and M. Szwarc, *Macromolecules*, **5**, 801 (1972).
(2) K. Shimada and M. Szwarc, *Chem. Phys. Lett.*, **28**, 540 (1974).
(3) A. Weller, private communication of yet unpublished results.
(4) N. Hirota, R. Carraway, and W. Schook, *J. Am. Chem. Soc.*, **90**, 3611 (1968).
(5) M. Itoh and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 1843 (1968).
(6) E. M. Kosower and Y. Ikegami, *J. Am. Chem. Soc.*, **89**, 461 (1967).
(7) M. Itoh and S. Nagakura, *J. Am. Chem. Soc.*, **89**, 3959 (1967).
(8) M. Itoh, *J. Am. Chem. Soc.*, **93**, 4750 (1971).
(9) M. Itoh, *J. Am. Chem. Soc.*, **94**, 1034 (1972).
(10) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
(11) J. Fergusson, *J. Chem. Phys.*, **28**, 765 (1958).
(12) J. N. Murrell and J. Tanaka, *Mol. . Phys.* **4**, 363 (1964).
(13) F. J. Smith, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 442 (1966).
(14) A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, **49**, 5066 (1968).
(15) J. B. Birks, *Nature (London)*, **214**, 1187 (1967).
(16) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970).
(17) T. Förster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).
(18) (a) N. J. Leonard, K. Golankiewicz, R. S. McCredie, S. M. Johnson, and I. C. Paul, *J. Am. Chem. Soc.*, **91**, 5855 (1969); (b) N. J. Leonard, H. Iwamura, and J. Eisinger, *Proc. Natl. Acad. Sci. U.S.*, **64**, 352 (1969).