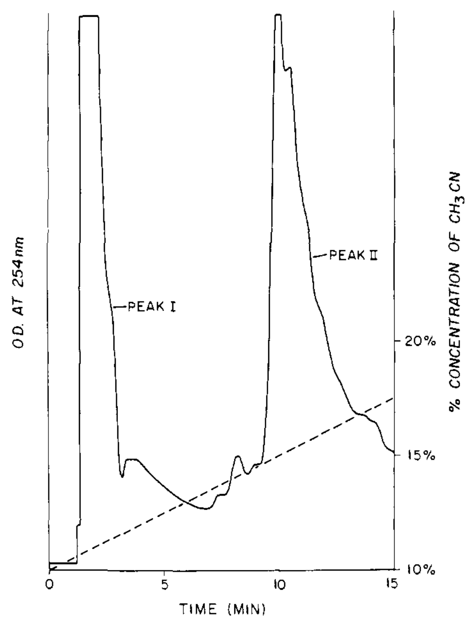

Figure 1. Absorption spectrum of the dimethoxytrityl group.

yribonucleotide with a defined sequence.

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Cyclization Dynamics of Polymers. 4. Electron Exchange between Chromophores on the Ends of Alkyl Chains: Diffusion-Controlled or Conformationally Controlled Cyclization?

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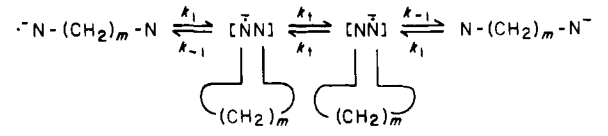
Several years ago Shimada and Szwarc[1,2] published an important series of papers investigating the rate of intramolecular electron exchange by ESR techniques in the molecules $N-(CH_2)_m-N^{-}\cdot$ and $PI-(CH_2)_m-PI^{-}\cdot$, where N is the 1-naphthyl substituent and PI represents the *N*-phthalimidyl moiety. Electron exchange occurs when the two end groups approach within a critical distance of one another. These papers have been frequently cited as representing the first experiments on the *dynamics* of end-to-end cyclization of hydrocarbon chains.[3,4] Dynamically controlled cyclization implies that the reaction occurs on every encounter—or in these examples on every other encounter since the electron can sit on either chromophore. On the other hand, if the electron transfer is inefficient, the reaction is preceded by a conformational equilibrium and is said to be under thermodynamic or conformational control. The purpose of this communication is to point out that for the reactions cited above, *there is no evidence that electron exchange is sensitive to chain dynamics. Rather, all evidence points to these reactions operating under conformational control.*

Scheme I



$$k_{ex}^{(1)} = k_1k_t/(2k_t + k_{-1})$$

The mechanism of these reactions can be represented in terms of Scheme I,[1b] where k_1 is the rate constant for diffusion together of the two chain ends, k_{-1} is that for their separation, and k_t is that for the electron exchange. Shimada and Szwarc point out that there are possibly many geometries for electron exchange possessing different intrinsic reactivities; k_t represents an average over these configurations.[1b] For this process to be dynamically (diffusion) controlled, electron transfer must be much faster than separation of the end groups, $k_t \gg k_{-1}$. The rate constant k_t is not infinitely fast. Since electron transfer is accompanied by solvent reorganization as well as changes in the counterion interaction, a nonnegligible activation barrier is anticipated[5] and found[1,2] for these reactions and their corresponding intermolecular counterparts:

$$1\text{-}C_2H_5\text{-}N^{-}\cdot + 1\text{-}C_2H_5\text{-}N \xrightarrow{k_{ex}^{(2)}} 1\text{-}C_2H_5\text{-}N + 1\text{-}C_2H_5\text{-}N^{-}\cdot$$

$$n\text{-}C_4H_9\text{-}PI^{-}\cdot + nC_4H_9\text{-}PI \xrightarrow{k_{ex}^{(2)}} n\text{-}C_4H_9\text{-}PI + n\text{-}C_4H_9\text{-}PI^{-}\cdot$$

In the electron exchange reaction between phthalimides, $k_{ex}^{(2)}$ values are much smaller than the diffusion limit.[2a] In addition, in five solvents $k_{ex}^{(2)}$ is independent of solvent viscosity. These experiments point to a rate-limiting electron-transfer step.

In the corresponding reaction between ethylnaphthalenes, $k_{ex}^{(2)}$ is much smaller than k_{diff},[1a] calculated from the Debye equation, for measurements in DME–2% HMPA, a very fluid solvent. In HMPA, these $k_{ex}^{(2)}$ values are only a factor of 3 smaller than the corresponding k_{diff} values (Table I). Shimada and Szwarc have results that suggest that electron transfer between naphthalenes in HMPA can occur over distances as large as 9 Å.[1] Thus the reaction cross section is much larger than the diffusion cross section for naphthalene in HMPA, and k_{diff} may be an order of magnitude larger than the values shown in Table I. Here again $k_{ex}^{(2)}$ is virtually independent of solvent viscosity.[1a]

The authors of these studies based their conclusion about dynamic control on a simple model calculation.[2] This model compares the experimental effective concentration, $C_{eff} = k_{ex}^{(1)}/k_{ex}^{(2)}$, to the corresponding concentration of two freely diffusing groups in a sphere whose radius is determined by the length r_{max} of the fully extended chain in the molecule from which $k_{ex}^{(1)}$ was determined. The idea is that r_{max} is the largest possible separation in $N-(CH_2)_m-N$. The average $\langle r \rangle$ is less than r_{max} and must lead to a higher effective concentration. These authors state "that the static model can never lead to the inequality $C_{eff} < C_{min}$, where $C_{min} = 1000/(V_{max}N_A)$, V_{max} being the volume of a sphere with radius equal to the length of extended chain. The dynamic model may account for the above inequality, and therefore our findings favor the dynamic model for the studied *intra*molecular electron transfer".[2b]

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Table I. Second-Order Rate Constants $k_{ex}^{(2)}$ for Electron Exchange in the Ion Radicals $1\text{-}C_2H_5N^{-}\cdot$ and $n\text{-}C_4H_9PI^{-}\cdot$[a, b]

T	η	$10^{-8}k_{ex}^{(2)}$	$10^{-8}k_{diff}$	T	η	$10^{-8}k_{ex}^{(2)}$	$10^{-8}k_{diff}$
$1\text{-}C_2H_5N^{-}\cdot$ in DME–2% HMPA[c]				$1\text{-}C_2H_5N^{-}\cdot$ in HMPA[c]			
−60	1.69	0.88	24	30	3.03	7.1	22
−30	0.93	2.3	58	15	4.24	5.0	15
0	0.61	4.2	100	0	6.23	3.0	10
E_a = 3.0 kcal/mol				E_a = 4.0 kcal/mol			
$n\text{-}C_4H_9PI^{-}\cdot$ in DME–2% HMPA				$n\text{-}C_4H_9PI^{-}\cdot$ in HMPA			
0	0.61	1.2	100	0	6.23	1.8	10
20	0.48	1.8	130	15	4.24	2.7	15
40	0.39	2.9	180	30	3.03	4.2	22
E_a = 3.6 kcal/mol				E_a = 5.2 kcal/mol			
$E_{a,diff}$ = 2.7 kcal/mol				$E_{a,diff}$ = 4.5 kcal/mol			

[a] 1-Ethylnaphthalene: N-butylphthalimide. Data from ref 1b and 2b. [b] Appropriate units are T in K, $k_{ex}^{(2)}$ and $k_{diff}^{(2)}$ in $M^{-1}\ s^{-1}$, η, solvent viscosity, in cP; $k_{diff}^{(2)}$ calculated from $k_{diff}^{(2)} = 8RT/3000\eta$. [c] DME is 1,2-dimethoxyethane; HMPA is hexamethylphosphoramide.

Table II. First-Order Rate Constants $k_{ex}^{(1)}$ for Electron Exchange in the Ion Radicals $N\text{-}(CH_2)_m\text{-}N^{-}\cdot$[a]

M	6	8	10	12	16	20	η
At 0 K							
$10^{-7}k_{ex}^{(1)}$(DME)[b]	2.5	1.3	1.1	0.88	0.56	0.42	0.61
$10^{-7}k_{ex}^{(1)}$(HMPA)	2.3	1.8	1.6	1.1	0.70	0.55	6.23
At 15 K							
$10^{-7}k_{ex}^{(1)}$(DME)[b]	3.3	1.7	1.5	1.3	0.70	0.52	0.51
$10^{-7}k_{ex}^{(1)}$(HMPA)	4.4	2.8	2.3	1.8	1.1	0.74	4.24

[a] $k_{ex}^{(1)}$ in s^{-1}, viscosity (η) in cP. [b] DME–2% HMPA.

As Halpern[6] has pointed out, this model is valid only for groups on the ends of a freely jointed chain. Hydrocarbon chains have fixed bond angles and limited rotational angles. Chains of this length have access to only a relatively small number of conformations. Thus while the chains serve to keep the end groups from separating, they also tend to keep them apart. Experimental values for C_{eff}, from the work of Mandolini and Illuminati,[7] are often much smaller than C_{min}. For their reactions, by an S_N2 mechanism, $k^{(2)}$ is 10 to 12 orders of magnitude slower than the diffusion-controlled rate constant.

Diffusion processes are sensitive to solution viscosity. Over limited viscosity domains, diffusion rates are inversely proportional to solution viscosity. This behavior has been observed for k_{diff}[8] for rotational diffusion,[9] for internal motion in hydrocarbon chains,[10] and for end-to-end cyclization dynamics probed by fluorescence techniques in polypeptides,[4c] polystyrene,[11] and poly(ethylene oxide).[12] Even more important is recent evidence that conformational transitions both in small molecules[13] and polymers[14] depend upon solvent viscosity. The definitive test as to whether $k_{ex}^{(1)}$ is sensitive to cyclization dynamics is whether it is sensitive to the viscosity of its environment.

For $PI\text{-}(CH_2)_m\text{-}PI^{-}\cdot$, Shimada and Szwarc point out that there is no sensitivity to solvent viscosity. For $N\text{-}(CH_2)_m\text{-}N^{-}\cdot$, electron exchange occurs slightly faster in HMPA than in DME–HMPA for all chain lengths and temperatures examined (Table II) in spite of the tenfold higher viscosity of the former solvent. These results are best explained in terms of a conformationally controlled reaction, which, because of ion-pair effects, has a larger reactive volume in HMPA than in DME.

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Hydrogenations with Molybdenum Hydrides Formed in the Reaction of Molybdenum Atoms with Tetrahydrofuran

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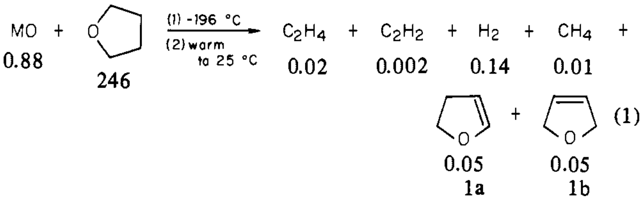
There have been several investigations in which the high reactivity of metal atoms[1] has been utilized to effect insertion of a metal into carbon–hydrogen[2,3] and carbon–carbon bonds.[2] Studies of the deposition of metal atoms into inert matrices in order to create slurries with high catalytic activity for processes such as hydrogenation have also been reported.[4] In this communication, we report the reaction of molybdenum atoms with tetrahydrofuran (THF) in which molybdenum hydrides are formed and may be used to effect hydrogenations of added olefins.

When Mo atoms, generated in an apparatus similar to that described by Dobson, Remick, Wilburn, and Skell,[5] are cocondensed with THF at −196 °C, the volatile products shown in eq 1 along with their millimolar yields have been identified.[6] An



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