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Chemically Induced Dynamic Electron Polarization. Ionic Strength and Radical Concentration Dependence[1]

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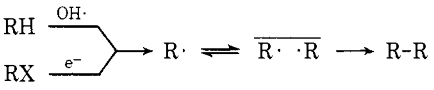
Abstract: The ionic strength effect on the polarization of radicals from radiolysis of acetate and malonate solutions is moderate. It appears that this effect is more pronounced at lower ionic strength. These findings are in qualitative agreement with theoretical predictions of Pedersen and Freed. It was also observed that polarization enhancement is independent of radical concentration.

Introduction

The intriguing question in the experimental study of the chemically induced dynamic electron polarization (CIDEP) phenomenon is whether this effect can be used to study intimate details of radical-radical interaction in solution. Of particular interest is to find out if larger and thus more experimentally accessible manifestations of various interradical interactions are reflected in the observables of a polarization study.

A brief outline of the current view of the magnetic polarization phenomena as it applies to the CIDEP of radicals produced by pulse radiolysis follows.



The radicals in a typical aqueous system are produced either by OH· abstraction reaction or hydrated electron reaction, where X is usually halogen. The addition of an OH· scavenger or e_{aq}^- scavenger can eliminate either of these two reactions. The use of N_2O effects conversion of e_{aq}^- to OH·, giving a clear-cut reaction system. Whether e_{aq}^- or OH· is the precursor can be determined by the study of initial relative signal intensities in the EPR spectrum of the radical in question. Our submicrosecond time-resolved EPR study of radicals from acetate and halo acetates is illustrative on this point.[2]

The radicals once produced encounter and undergo spin-selective reaction. Usually the singlet-state radical pairs preferentially react, leaving the excess of radical pairs with triplet-spin character. These remaining radicals undergo diffusive displacements, at which time singlet-triplet mixing can occur.[3] The polarization process is completed by the exchange (J) when the radicals are close enough (re-encounter). Any change in attraction or repulsion between radicals may have an effect on the electron-spin polarization, which is generated in the region where radicals are attracted or repulsed. In their recent theoretical work, Pedersen and Freed consider the effect of ionic interaction among charged radicals.[6] The effect of the ionic strength of the solution on the polarization of radicals depends on the size of exchange (J). The effect of the Coulomb force on the polarization is smaller for larger values of ex-

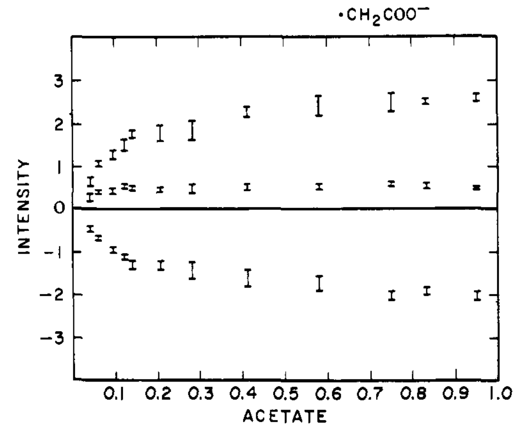


Figure 1. EPR line intensities of $\cdot CH_2COO^-$ radical in aqueous acetate solution (pH ~7) 2 μs after the 100-ns electron pulse (0.5-μs gate) as a function of acetate concentration. EPR peak heights in this and other figures are given in arbitrary units. The concentration unit is molarity.

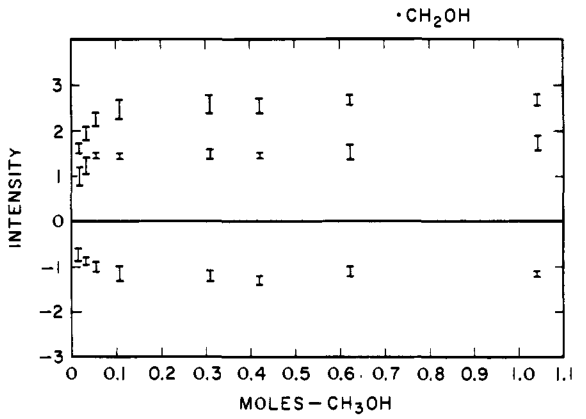


Figure 2. EPR line intensities of $\cdot CH_2OH$ radical in aqueous methanol as a function of methanol concentration. Experimental parameters are the same as in Figure 1.

change (J). Estimated change in polarization for repulsive forces (like charge on radicals) is less than 50% for larger J. For small values of exchange (J) repulsive forces are expected to diminish polarization by a factor of 5–50 and attractive forces increase polarization by that amount. In the case of nonspherical radicals and small exchange, the ionic effect is expected to be more pronounced at lower ionic strength.[6]

No study of ionic effects on polarization has been reported. The analysis of ionic strength effect on polarization may provide many details of exchange interaction between radicals, however at this time only a semiquantitative examination of ionic effects has been possible. In this work, we examined the effect of ionic strength on the polarization of radicals from radiolysis of aqueous solutions of acetates and malonates. Also the dependence of polarization enhancement on the radical concentration was studied.

The polarization enhancement should be proportional to the radical concentration, and it is usually defined by

$$V = (\rho^*/\rho_{eq})\beta T_1 \qquad (1)$$

where V is the polarization enhancement, ρ^*/ρ_{eq} is the intrinsic enhancement, T_1 is the electron spin–lattice relaxation time of the radical in question, and β is the inverse of radical half-life and is defined

$$\beta = k_2'n_0 \qquad (2)$$

where k_2' is the second-order rate constant for reaction of radicals and n_0 is the radical concentration after the electron pulse. The experimentally observed enhancement V_{expt} will be related to enhancement at the end of the electron pulse V (time zero) by

$$V_{expt} = Vn(t)/n_0 \qquad (3)$$

where radical concentration at time t after the electron pulse is

$$n(t) = n_0/(1 + \beta t) \qquad (4)$$

Since all the enhancement measurements were carried out 2–3 μs after the electron pulse, there is 10–20% difference between n_0 and $n(3\ \mu s)$, except in the limit of very large initial radical concentrations, e.g., $n_0 \simeq 10^{-3}$ M. While the $n(t)/n_0$ ratio can be affected by ionic strength, we expect this effect to be smaller than our experimental error. It should be noted that ionic strength will have an effect on k_2' of charged radicals and can in this way change enhancement by changing the radical half-life.[7]

Experimental Section

Time-resolved EPR experiments were carried out using 3-MeV electrons from the Van de Graaff accelerator.[4]

The aqueous solutions of sodium acetate, disodium malonate, and methanol were prepared using deionized water. pH was near neutral; pK_a's of radicals from acetate and malonate are 4.5 and 5.7, respectively.[8] N_2O was used to effect conversion of e_{aq}^- to OH. All compounds were obtained from commercial suppliers and used without purification.

In the study of ionic effects on polarization, the measurement of signal intensities was performed on the spectra obtained at a fixed time window after the electron pulse. The only variable in these experiments was the concentration of acetate, malonate, and lithium perchlorate.

In the study of polarization enhancement dependence on the radical concentration, the signal intensities in the EPR spectra of the radicals in question were monitored at a fixed time window after the electron pulse. The amount of radicals produced per pulse was varied by changing the pulse width of the electron beam while keeping the beam intensity constant. The pulse width was varied from 50 to 500 ns. This method was more reproducible than the variation of pulse intensity with fixed pulse width. All data represent experimental scatter of several series of runs. All EPR intensities represent peak heights. Since all data are obtained at the same time window after the electron pulse, the line width should be identical.

Results and Discussion

Ionic Effects. The peak intensities of the three lines of the $\cdot CH_2COO^-$ radical as a function of sodium acetate concentration are shown in Figure 1.

The intensities of the low-field line (emission), central line (not polarized), and high-field line (enhanced absorption) are plotted with the experimental scatter as indicated. The central line is a measure of radical concentration. The polarized peak intensities increase with increasing concentration of acetate (ionic strength). There is a more pronounced change at lower acetate concentrations, while above 0.1 M acetate we observe only a slight increase in polarized peak heights. The sharp drop in signal intensity below 0.1 M acetate appears to be due in part to the incomplete scavenging of OH·. We suspect that at lower acetate concentrations local exhaustion of substrate and alternate pathways for OH· destruction are responsible for the decrease in the acetate radical production.[9] This is evidenced by the drop in the intensity of the central line.[10] This is also exhibited by other (uncharged) radicals. Notably, $\cdot CH_2OH$ radical from aqueous methanol (Figure 2). The ionic effect is also contributing to the decrease in polarization below 0.1 M acetate. This was checked in the experiments where acetate concentration was kept constant and the ionic strength of the solution was varied by the addition of lithium perchlorate (Figure 3). Clearly, while the central line remains constant the

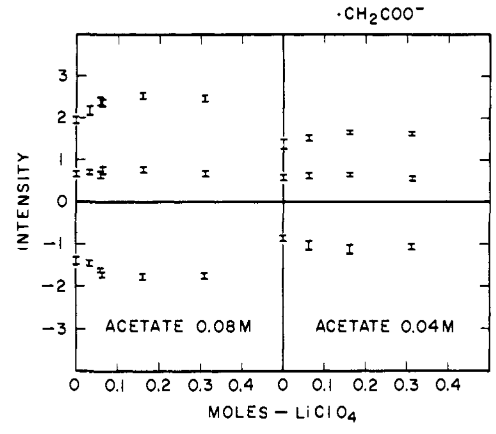


Figure 3. EPR line intensities of $\cdot CH_2COO^-$ radical in aqueous acetate solution as a function of lithium perchlorate concentration. Other parameters are the same as in Figure 1.

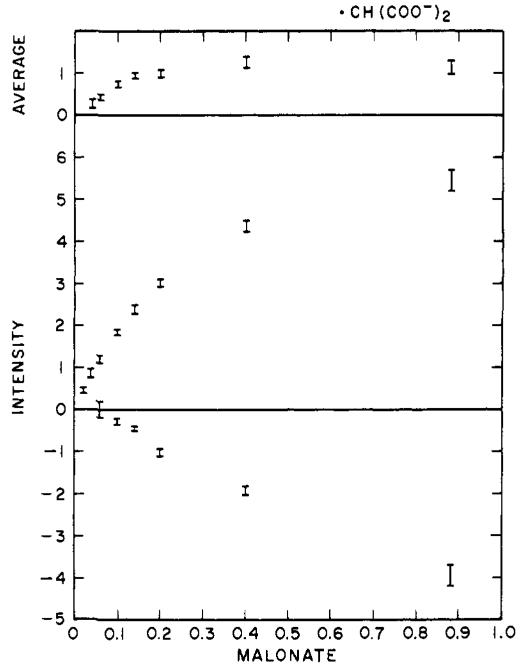


Figure 4. EPR line intensities of $\cdot CH(COO^-)_2$ radical in aqueous malonate solution. Average of low- and high-field lines plotted above. Other parameters are the same as in Figure 1.

intensities of the polarized low- and high-field lines are changed. There is a leveling off at higher perchlorate concentrations. In these experiments it should be noted that the concentration of acetate used is too small to capture all ·OH. Thus the observed peak intensities level off, with increase in ionic strength, at values depending on the concentration of acetate used. In the 0.04 M acetate (Figure 3), a smaller number of radicals is produced and the starting ionic strength of the solution is less than in 0.08 M acetate. Also note that the change in polarized peak heights is more gradual in the 0.04 M case as compared to the 0.08 M case. Experiments with higher acetate concentration and perchlorate concentration from 0–1 M show no change in peak intensities.

Similar behavior is found in doubly charged radicals from malonate (Figure 4). In this case the average (top, Figure 4) of the low- and high-field lines is an indication of radical concentration. The ionic effect is appreciably larger in malonate. (The ionic strength goes up to 3 at 1 M malonate, while the ionic strength in 1 M acetate is only 1.) Also, the bimolecular rate constant for radical disappearance is smaller than that for radicals from acetate (Table I).[8]

Table I[a]

Concn, M	$k_2'/\epsilon l^b$	% error
Acetate		
0.05	2.74×10^5	±1.15
0.5	3.11×10^5	±0.47
1	3.29×10^5	±0.48
Malonate		
0.05	6.06×10^3	±0.49
0.5	2.13×10^4	±0.55
1	2.76×10^4	±0.92

[a] We are indebted to Drs. S. Gordon, B. G. Saunders, and C. D. Jonah of the Chemistry Division of the Argonne National Laboratory for these measurements. [b] Where ϵ is the extinction and l is the optical cell length. Units of k_2' are $M^{-1}\ s^{-1}$.

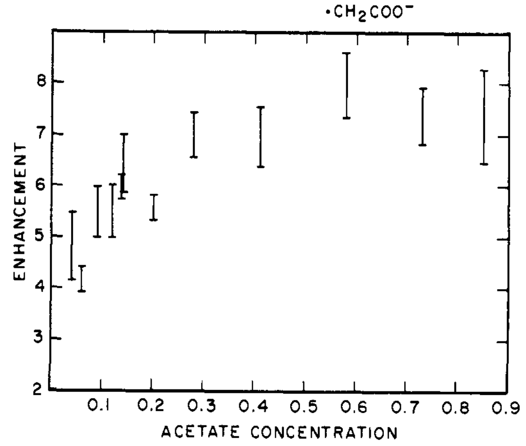


Figure 5. Polarization enhancement, $V_{expt} = (H_L - H_H)/(H_L + H_H)$ where H_L and H_H are the EPR intensities of low-field and high-field lines, respectively, as a function of acetate concentration.

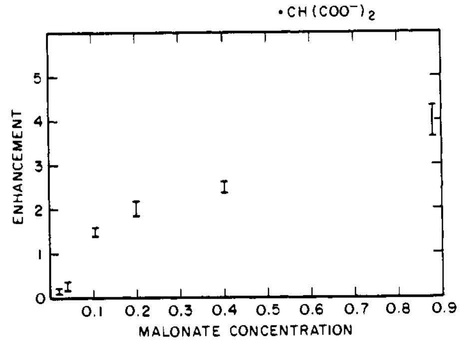


Figure 6. Polarization enhancement as a function of malonate concentration.

The polarization enhancement in malonate radicals is less than in acetate radicals, thus at low malonate concentration the low-field line is in absorption and not emission, since the contribution of unpolarized radical intensity is larger.[12] As in the radical from acetate, the intensity drop below about 0.2 M is caused by a combination of incomplete OH· scavenging and ionic effects. The incomplete OH· reaction is evidenced by the smaller average of the low- and high-field lines. In Figures 5 and 6 polarization enhancement is plotted vs. the concentration of acetates and malonates, respectively. As can be seen, enhancement reaches a constant value with acetate and probably also in malonate at higher concentrations.

The independent determination of rate-constant (k_2') dependence of the ionic strength of the solutions of acetate and malonate allow us to make more definite, albeit only semi-

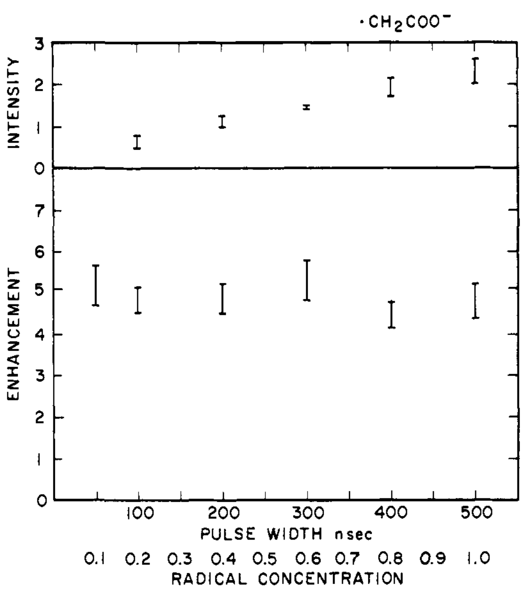


Figure 7. Polarization enhancement in $\cdot CH_2COO^-$ radical as a function of electron pulse width (radical concentration) in 0.2 M acetate. Data obtained 3 μs after the electron pulse (0.5-μs gate). At the top is the plot of the central-line intensity. The radical concentration unit is ~5 × 10^{-4} M.

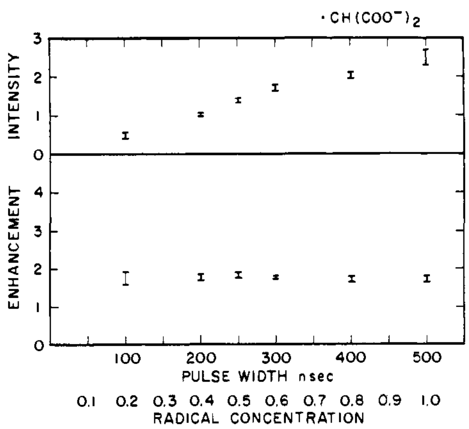


Figure 8. Polarization enhancement in $\cdot CH(COO^-)_2$ radical as a function of electron pulse width (radical concentration) in 0.4 M malonate. At the top is the plot of the average of the high- and low-field lines of the radical. Other experimental parameters are the same as in Figure 7.

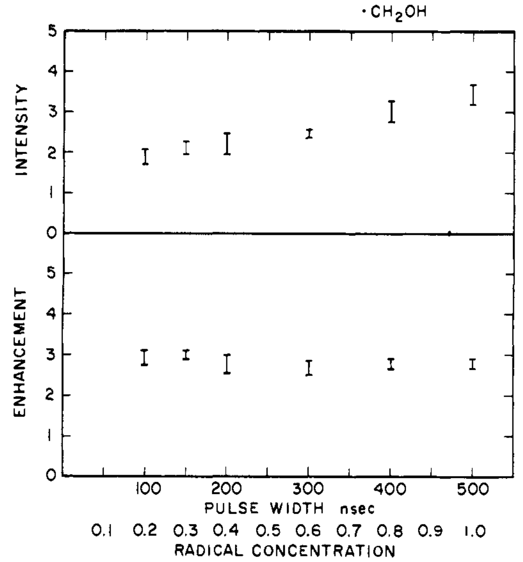


Figure 9. Polarization enhancement in $\cdot CH_2OH$ radical as a function of electron pulse width (radical concentration) in 2.4 M methanol. Other experimental parameters are the same as in Figure 7.

quantitative, conclusions regarding the ionic strength effect on the polarization. The polarization in acetate radical changes ~30%, while the change in the rate constant is only ~10%. Thus, it appears that the larger contribution to the polarization is the ionic effect on polarization (ρ^*) and not the ionic effect on the radical half-life (k_2'). The experiments with lithium perchlorate (Figure 3) are particularly illustrative of the larger ionic effect on polarization at lower ionic strengths. In the case of the radical from malonate, the smaller polarization enhancement and smaller second-order rate constant combine to make the same deduction less quantitative. Nevertheless, the trends in malonate radical are similar to that of acetate radical.

Polarization Enhancement and Radical Concentration. In a previous study, the comparison of two steady-state and pulse experiments at lower radical concentrations seems to indicate that the observed enhancement is proportional to radical concentration.[11] Our study of polarization enhancement dependence on the radical concentration produced unexpected results. The polarization enhancement as a function of relative radical concentration (pulse width) in radicals from methanol, acetate, and malonate is shown in Figures 7, 8 and 9.

As can be seen by the plot of the intensity of the central line for radicals from methanol and acetate and the average of low- and high-field lines for malonate, the radical concentration was usually changed by at least a factor of five. In all three cases studied we have observed that polarization enhancement is independent of radical concentration. While the experimental error is obviously considerable, it should not mask the substantial change of polarization enhancement expected with the large change in radical concentration. Especially in the case of acetate, where the enhancement is largest, it is hard to believe that experimental error could indeed obscure any substantial change in enhancement. The initial acetate radical concentration varies from ~5 × 10^{-4} M for the largest dose (500-μs pulse width) to ~10^{-4} M for the smallest dose (100-μs pulse width). (The measured half-life varies from ~2 to 10 μs.) Taking into account eq 4 for n (3 μs) where the observation was carried out we would expect the fivefold increase in radical concentration to result in an almost threefold increase in the observed enhancement (V_{expt} at 3 μs). The polarization quenching and/or transfer might conceivably cause deviation from linearity at higher radical concentrations.[13] This is under investigation.

At this time we are also considering the possibility that initial nonuniform spatial distribution of radicals may be responsible for our observations.[14] The polarization enhancement observed at a later time (5-20 μs) might reveal this. However, a combination of smaller signal enhancement and lower radical concentration makes such observations more difficult. Presently we are conducting experiments which we hope will clarify our speculations. The detailed examination of both the submicrosecond (100 ns-1 μs)[15] and microsecond (1-30 μs) domain is being undertaken.

Acknowledgment. We wish to express our thanks to K. W. Johnson and B. E. Clifft for their efforts in instrument development. We acknowledge R. H. Lowers for his operation of the Argonne Chemistry Division Van de Graaff accelerator. We are indebted to Drs. C. D. Jonah, M. S. Matheson, and M. C. Sauer for discussions.

References and Notes

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(7) The second-order rate constant for radical reaction k_2' consists of two parts, k_2 and F, where k_2 is half of the second-order rate constant for new bimolecular collisions of radicals and F is the probability of reaction per collision. Both k_2 and F are affected by the ionic strength. We cannot separate these two effects. For detailed discussion see ref 6.

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(10) In the time-resolved study of $\cdot CH_2COO^-$ radical, smaller enhancement and reduced intensity of the central line in a 0.01 M solution of acetate was observed.[11]

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(12) At low malonate concentrations the absorption of the low-field line of malonate is changed to emission at longer times ($\gtrsim 3$ μs) after the pulse.

(13) When $T_1\beta \ll 1$, the radicals will lose their polarization before they collide with new radicals. However, when the larger concentration of radicals is produced ($n_0 \sim 10^{-3}$ M and $\beta \sim 10^6$) the above may no longer be true (see ref 6).

(14) We speculate that part of the polarization that we observe at 2–3 μs after the electron pulse may be created before uniform radical distribution is reached. With the higher dose we create more radicals, but the number of radicals that can participate in the polarization process (at short times) may be approximately constant, since they are contained in separated spurs. These ideas would accomodate Fessenden's results,[11] which were obtained at lower radical concentrations and later times (8–10 μs after the electron pulse), since the nonuniform radical concentration would affect only the early polarization production (at times <1 μs) which would disappear in several microseconds ($\sim 3T_1$).

(15) Recent instrument improvements allow us to obtain EPR spectra as close as 50–100 ns after the electron pulse.

Studies on the Formation of Topological Isomers by Statistical Methods

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Contribution from the Department of Organic Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel. *Received August 11, 1975*

Abstract: To improve the statistical synthesis of topological isomers, the factors which determine the amount of threading of linear chain molecules in macrocyclic rings were studied in detail. Polymeric rotaxanes were prepared by statistical threading of poly(ethylene glycols) in "crown polyethers". The compounds were mixed and heated, and the equilibrium was "frozen" by polymerization of the chains to polyurethanes by adding naphthalene-1,5-diisocyanate. The amount of threaded rings was determined after selective separation of the components on silica gel. The effects of the molar ratios of rings to chains, length of chain, radius of the ring, volume of the system, and temperature on the amount of threading were studied. Based on statistical consideration of ratio of reactants and volume of the system, and on geometrical factors, the following mathematical expression was derived to show the effect of these factors on the amount of threading: $N = k[m_e m_g(1 - e^{-n_e/\pi n_g})n_e n_g{}^{\beta}\theta]/V$ where N is the number of threadings, m_e and m_g are the number of moles of rings and chains respectively, n_e and n_g are the number of atoms in rings and chains, V is the total volume, and θ is the threading angle, which depends on the radius of the ring (r) and diameter of the chain end (d) and is determined by $\cos\theta = d/2r$. The constants β and k which suit the results are $\beta = 1.3$ and $k = 0.195$. There was good correlation between this mathematical model, the experimental results, and molecular models imitating the ring–chain threading system. The optimal conditions found for the threading system was utilized for the preparation of [2]-[ω,ω′-di(*O*-trityl)poly(ethylene glycol) 400]-[dibenzo-58.2-crown-19.4]rotaxane in relatively high yield (15%). Similar yield was obtained by polymerizing ethylene oxide by the di(potassium alkoxide) derivative of tetra(ethylene glycol) in the presence of "crown" polyether. Chromatographic and spectral evidence, as well as hydrolysis of the blocking trityl groups, was used to prove the structure of the rotaxane. The thermal decomposition of the rotaxane was investigated at 130–190 °C. The following equilibrium was found to exist: rotaxane $\rightleftharpoons$ ring + chain (k, k'), and the reaction constants were determined. The stability of the rotaxane was explained, taking into consideration the data obtained for the heat of decomposition (9.5 kcal/mol) and the activation energies of the decomposition and threading processes (15.9 and 3.4 kcal/mol, respectively). The higher activation energy needed for the decomposition was explained by the dipole–dipole interactions which exist between the ethylene oxide units in the threaded chain and those in the ring.

Since the first synthesis of a catenane by Wasserman[1] in 1960, only few topological isomers—catenanes and rotaxanes—have been prepared. Several approaches were developed, including the directed synthesis,[2] which needs many consecutive reaction steps, the statistical method,[1,3] which is relatively much simpler to perform but produces very low yields of the topological isomer, and the Möbius-strip method,[4] by which the formation of the desired product was demonstrated mass spectrometrically, although it has not yet been isolated. Variation of the statistical method taking advantage of orientation of polar reactants at interfaces was utilized for the synthesis of polycatenanes.[5]

Besides Wasserman, the statistical threading of linear chain molecules in macrocyclic ring molecules was used by Harrison,[3] who synthesized several rotaxanes. The rings in these cases were built of 24–33 atoms, and the yields were between 0.0013–1.6%. Harrison investigated the stability of the various rotaxanes and the effect of ring size on their yields.

Frisch and Wasserman[6] proposed an expression for estimating the amount of threading of linear chain molecules through macrocyclic rings. The yield predicted for the synthesis of the catenane by Wasserman[1] was 4%, compared with the 1% yield which was found experimentally.

As a result of the difficulties in the preparation of topological isomers, very little is known about their physical properties. Particularly interesting are their colligative properties which are determined by the number of molecules. Until now, only one measurement has been reported,[7] which shows that a [3]-catenane having a "tight" structure behaves as if it was one molecule.

The present study was undertaken to achieve a fuller understanding of the statistical threading of linear molecules in macrocyclic rings, and to utilize the data thus obtained to improve the statistical synthesis of a rotaxane.

Statistical Threading of Linear Chains in Macrocyclic Rings. A "threading system" was developed with the purpose of in-