tive conclusion that Cl is much easier (*i.e.*, factor of ~10 per bond) to replace than H in CH_3Cl. The bond strength of the C–H bond (97.4 kcal/mole) is considerably larger than that of C–Cl (83.5 kcal/mole) in CH_3Cl,[34] and the substitution of Cl for H is certainly endothermic by nearly 15 kcal/mole. However, since the threshold energies for both substitution reactions are probably 35–50 kcal/mole, it is not clear that a more endothermic reaction is necessarily unfavored in its yield. Further experiments with other parent molecules are certainly needed for assessment of the various factors controlling the quantitative yields of hot Cl substitution reactions.[16,24]

These experiments with energetic Cl atom reactions with CH_3Cl, have, however, established or confirmed several important characteristics of such substitution reactions: (a) the nuclear reactions $Cl^{37}(n,\gamma)Cl^{38}$ and $Ar^{40}(\gamma,p)Cl^{39}$ produce chlorine atoms whose chemical behavior with CH_3Cl can be very plausibly described as the chemical reactions of neutral, ground-state atoms with excess kinetic energy; (b) Cl atoms react with methyl chloride in high kinetic energy reactions to form CH_3Cl and CH_2Cl_2 by substitution for Cl and H, respectively (the hot yields of these substitution products account for only a small per cent of the total energetic chlorine produced when the reactions are carried out in the gas phase, about 3.1% as CH_3Cl and 0.7% as CH_2Cl_2); (c) the hot yields of both substitution products can be substantially reduced by moderating the kinetic energy in collisions with inert helium or neon (the moderating efficiency of CH_3Cl for Cl is about three times greater than that of neon, consistent with a large fraction of highly inelastic collisions for the polyatomic molecule; neon, whose mass is closer to that of Cl, is 2.5 times more efficient as a kinetic energy moderator than helium).

(34) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. 1, Princeton University Press, Princeton, N. J., p 24.

Reactions of Methyl Radicals with Aromatic Hydrocarbons. Effect of Conformation and Carbon–Hydrogen Orientation upon the Rate, the Activation Energy, and the *A* Factor

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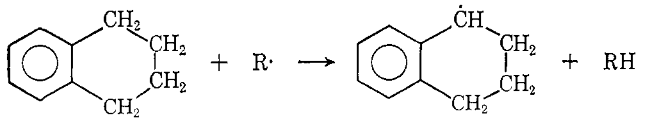
Abstract: Competition between $RH + CH_3\cdot \rightarrow R\cdot + CH_4$ (k_1) and $C_6H_5CH_3 + CH_3\cdot \rightarrow C_6H_5CH_2\cdot + CH_4$ (k_T) was investigated in the liquid phase over a temperature range 0–95°. Methyl radicals were produced by the photolysis of azomethane, and tritiated toluene, $C_6H_5CH_2T$, was used to distinguish between the products of the reaction of RH and toluene. The following compounds were studied: *o*-, *m*-, and *p*-xylenes, mesitylene, ethylbenzene, 1,2-diphenylethane, indan, tetralin, cumene, *p*-*t*-butylcumene, cyclohexylbenzene, diphenylmethane, and triphenylmethane. The results show that the reactivity is governed primarily by the nature of the carbon–hydrogen bond: tertiary > secondary > primary. Within each series the ratio A_1/A_T (per active H atom) remains essentially constant if the effect of conformation is taken into account. Changes in reactivity are caused by changes in the respective activation energies, again corrected for the effect of conformation which introduces an additional term, Δ, in the observed activation energy. It was found that the abstraction of a tritium atom requires 2.7 kcal/mole higher activation energy than the abstraction of hydrogen.

Tetralin and indan are unusually reactive toward radicals.[1,2] It seems that the process



is much faster than other analogous reactions involving a secondary hydrogen atom located on a carbon α to the benzene ring. These observations were confirmed by our past study of the H abstraction[3]

$$RH + CH_3\cdot \longrightarrow R\cdot + CH_4 \qquad k_1$$

where RH = toluene, the xylenes, mesitylene, ethylbenzene, cumene, indan, and tetralin. Those results provided the ratios k_1/k_T, where k_T refers to the reaction

$$PhCH_3 + CH_3\cdot \longrightarrow PhCH_2\cdot + CH_4 \qquad k_T$$

The experiments were performed in the liquid phase at one temperature only (65°) and led us to the following conclusions. Tetralin has a "normal" reactivity; *i.e.*, the ratio $k_1(\text{tetralin})/k_T$(per active hydrogen atom) has a value similar to that found in the aliphatic series when a secondary hydrogen is compared with a primary one. However, ethylbenzene and cumene are less reactive than anticipated, since the most probable conformation of these molecules is unfavorable for the H abstraction. We expected, therefore, that the "abnormally" low relative reactivity of ethylbenzene and cumene should be reflected in the relatively high activa-

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(1) G. A. Russell, *J. Am. Chem. Soc.*, 78, 1047 (1956).

(2) A. L. Williams, A. E. Oberright, and J. W. Brooks, *ibid.*, 78, 1190 (1956).

(3) J. A. Meyer, V. Stannett, and M. Szwarc, *ibid.*, 83, 25 (1961).

Table I. Sample Data

	Sample	
	10 ml of tritiated toluene, sp act. = 0.1 mCi/ml	5 ml of tritiated toluene, sp act. = 0.2 mCi/ml, 5 ml of *o*-xylene
Azomethane concn, *M*	3.4×10^{-3}	3.4×10^{-3}
Reaction conditions	12-hr ultraviolet photolysis at 75°	
Product gas pressure in chamber, mm	0.815	1.048
Molecules in chamber	1.475×10^{19}	1.897×10^{19}
Rel methane % from mass spectrometer	51.72	52.68
Methane molecules in chamber	7.63×10^{18}	9.99×10^{18}
Net mV/min from electrometer	6.4	6.1
Counts per minute per mol of methane	$1.475 \times 10^8 \times 2 = 2.950 \times 10^8$	1.074×10^8
k_2/k_1	$\left(\frac{2.950 - 1.074}{1.074}\right)(1.135) = 1.983$	

tion energy of the respective abstraction process, whereas a "normal" activation energy was predicted for tetralin.

Experimental Section

Methyl radicals were generated by the photolysis of azomethane using a high-pressure mercury lamp (AH-6) as the source of actinic light. The technical details were described elsewhere.[4] The azo compound was dissolved in tritiated toluene or in its mixture with the investigated hydrocarbon and then photolyzed at constant temperature.

Toluene tritiated solely in the side chain was prepared by the New England Nuclear Corp. The original compound had an activity of 500 mCi/ml and was a 100-fold diluted with purified, nonactive toluene. From this stock solution 8 ml was removed, whenever needed, and further diluted in a 200-ml volumetric flask with purified toluene. This liquid, having a specific activity of 0.2 mCi/ml, was used in all the experiments. The self-radiolysis of the hot sample may produce traces of hydrogen and methane of high specific activity. It is necessary therefore to purge the toluene by bubbling through it a mixture of $CH_4 + H_2$, while the liquid is refluxed, and check eventually the activity of such a mixture of gases after it has been circulated for a while through the toluene. The hydrocarbon is suitable for experiments only when no activity is observed in the gaseous mixture.

In each run eight ampoules were simultaneously photolyzed. Two were "blanks" containing only the radioactive toluene (10 ml) and the azo compound ($\sim 10^{-3}$ *M*); six were mixtures of the investigated aromatic hydrocarbon and the radioactive toluene having a total volume of 10 ml. All the samples were carefully deaerated on a high-vacuum line and sealed in cylindrical Pyrex ampoules, each equipped with a break-seal. The top of each ampoule was wrapped with aluminum foil to prevent the photolysis of the vapor; the ampoules were immersed in a constant-temperature bath and irradiated for 8–24 hr.

Analysis of the products of the photolysis was performed on a high-vacuum line,[4b] and the gases ($CH_4 + N_2$) were collected in a small flask. This was linked to an evacuated 500-ml ionization chamber into which the gas was expanded, and the chamber was then pressurized with Matheson P-10 gas (90% A + 10% CH_4). The radioactivity was determined by means of a Cary Model 32 vibrating reed electrometer using the rate-of-charge method. The background activity of the ionization chamber was checked before each run. The chamber was first evacuated and filled with P-10 gas, and then the background was counted.

The pressure of the remaining gas (equal to its pressure in the ionization chamber) was measured with a McLeod gauge, the gas pumped into an evacuated collection stopcock, and its composition, *i.e.*, the CH_4/N_2 ratio, determined by means of a Consolidated Electrodynamics Corp. Model 21-620 mass spectrometer. Thus, the amount of CH_4 introduced into the ionization chamber could be calculated giving, therefore, its specific activity. A typical set of data are shown in Table I. Further details of the procedure are described elsewhere.[5]

Results

Photolysis of azomethane in a liquid hydrocarbon leads to the following reactions.

$$CH_3N_2CH_3 + h\nu \longrightarrow 2CH_3\cdot + N_2$$

$$2CH_3\cdot \text{ (in a cage)} \longrightarrow C_2H_6$$

$$CH_3\cdot \text{ (out of cage)} + C_6H_5CH_2T \longrightarrow$$
$$CH_4 \text{ (or } CH_3T) + C_6H_5CH_2\cdot \quad k_T$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \quad k_1$$

Under the conditions of our experiments, the bimolecular combination of $CH_3\cdot$ and their reaction with benzyl or $R\cdot$ radicals are negligible[4] and need not be considered. The ratio of the specific activity of CH_4 to that of toluene (in the absence of RH) measures the isotope effect. The results, covering the range 0–95°, are given in Table II and presented graphically in Figure 1. The activation energy $E_{Tr} - E_H$ is equal to 2.7 kcal/mole, the ratio of the preexponential factors being close to unity. Unfortunately, the specific activity of liquid toluene was determined in a scintillation counter, whereas that of methane was measured in the ionization chamber. The lack of a direct comparison could introduce an error of up to 50% in A_{Tr}/A_H; however, this does not affect $E_{Tr} - E_H$.

Table II. Isotope Effect in the Reaction $PhCH_3 + CH_3\cdot \rightarrow PhCH_2\cdot + CH_4$[a]

Temp, °C	No. of expts	Sp act. of CH_4, dpm mole^{-1} $\times 10^{-8}$	$\frac{k_H}{k_{Tr}} = \frac{\text{sp act. of toluene}}{3 \times \text{sp act. of } CH_4}$
0	9	1.03	152
25	6	1.52	103
50	6	2.18	72
75	8	2.96	53
95	7	3.67	43
		$E_{Tr} - E_H$ = 2.7 kcal/mole	$A_{Tr}/A_H \sim 1.0$

[a] Specific activity of toluene ($C_6H_5CH_2T$) = 4.7×10^{10} dpm mole^{-1}.

In the presence of an aromatic hydrocarbon (RH), the specific activity of methane decreases, and the ratio k_1/k_T may be calculated from the relation

$$k_1/k_T = (X_T/X_{RH})\{(\text{sp act. of } CH_4)_{\text{blank}} -$$
$$(\text{sp act. of } CH_4)_{\text{expt}}\}/(\text{sp act. of } CH_4)_{\text{expt}}$$

where X_T/X_{RH} denotes the molar ratio of tritiated toluene to RH. All the substrates in the present study

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(4) (a) C. Steel and M. Szwarc, *J. Chem. Phys.*, **33**, 1677 (1960); (b) M. Gazith and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 3339 (1957).

(5) A. E. Eachus, Ph.D. Thesis, State University College of Forestry, Syracuse, N. Y., June 1964.

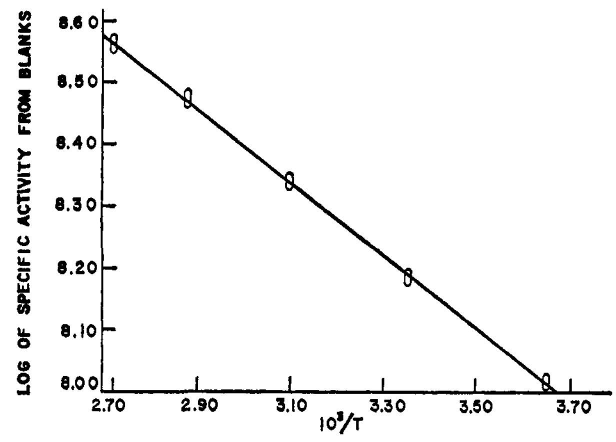

Figure 1.

were investigated within the range 30–50 mole % of substrate, with the exception of the most reactive compound, triphenylmethane, where a concentration of 8 mole % was used. k_l/k_T should be independent of X_T/X_{RH},[6] and this was verified for cumene in the liquid phase at 90° over a wide concentration range. The pertinent results are shown in Table III, and the data obtained from a corresponding study of the gas-phase system are also given. The temperature dependence of k_l/k_T within the range 0–95° is tabulated in Table IV.

Table III. Dependence of k_l/k_T on the Mole Ratio of Toluene/Cumene at 90°

Toluene/cumene mole ratio	k_l/k_T per active H atom
Liquid phase	
5.21	10.0
2.96	11.4
1.72	10.3
1.31	11.8
0.84	11.0
0.33	11.4
Gas phase^a (P_{total} ~ 400 mm)	
5.21	8.0
2.94	7.4
1.72	7.8
1.31	8.5(?)

^{a} The low volatility at 90° of toluene–cumene mixtures containing >40 mole % of cumene prevented study of a wider concentration range.

The xylenes and mesitylene exemplify the benzylic hydrocarbons possessing primary C–H's, ethylbenzene and 1,2-diphenylethane exemplify those with a secondary C–H, and cumene, *p-t*-butylcumene, and cyclohexylbenzene represent those with a tertiary C–H. In addition, indan and tetralin are the examples of secondary C–H's having fixed conformation. Finally, diphenyl- and triphenylmethane were added to the investigated compounds as examples of hydrocarbons yielding radicals of higher resonance stability. All the investigated hydrocarbons were carefully purified, and their degree of purity was found satisfactory by vpc analysis.

Some representative Arrhenius plots of log k_l/k_T are shown in Figure 2, and the activation energies, $E_l - E_T$, and the respective ratios of the preexponential factors, A_l/A_T, are given in Table V.

Table IV. Relative Rate Constant of H Abstraction per Active H Atom

Hydrocarbon	No. of reactive H atoms	Temp, °C	No. of expts	k_l/k_T per active H atom
o-Xylene	6	0	2	1.11
	6	25	2	1.06
	6	50	2	1.03
	6	75	2	1.00
	6	95	2	0.98
m-Xylene	6	0	3	1.08
	6	25	2	1.06
	6	50	2	1.02
	6	75	4	1.00
	6	95	2	0.96
p-Xylene	6	0	2	1.26
	6	25	2	1.20
	6	50	2	1.16
	6	75	3	1.11
	6	95	2	1.08
Mesitylene	9	0	3	1.18
	9	25	2	1.09
	9	50	4	1.02
	9	75	4	0.97
	9	95	4	0.93
Ethylbenzene	2	0	2	5.54
	2	25	1	5.01
	2	50	3	4.63
	2	75	3	4.21
	2	95	2	3.96
1,2-Diphenylethane	4	0	1	5.44
	4	50	2	4.34
	4	95	2	3.74
Indan	4	0	2	15.0
	4	25	2	11.4
	4	50	2	9.2
	4	75	2	9.0
	4	95	2	8.0
Tetralin	2	0	2	50.6
	2	25	2	33.3
	2	50	2	28.0
	2	75	1	20.8
	2	95	2	18.2
Cumene	1	0	4	19.7
	1	25	1	17.2
	1	50	4	14.5
	1	75	4	12.8
	1	95	3	11.9
p-t-Butylcumene	1	0	2	24.0
	1	50	2	16.9
	1	95	1	12.9
Cyclohexylbenzene	1	0	2	15.9
	1	25	2	13.6
	1	50	2	12.3
	1	75	2	11.1
	1	95	2	10.1
Diphenylmethane	2	0	3	19.3
	2	25	2	17.2
	2	50	2	16.3
	2	75	2	13.6
	2	95	1	11.7
Triphenylmethane	1	0	2	170
	1	25	2	84.3
	1	50	4	77.1
	1	75	2	72.3
	1	95	2	62.4

Isotope Effect. The method used in our studies was previously utilized by Berezin and Dobis[7] for investigating competition between a series of hydrocarbons, such as heptane, cyclohexane, cyclopentane

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(6) W. J. Cheng and M. Szwarc, *J. Phys. Chem.*, **71**, 2726 (1967).

(7) I. W. Berezin and O. Dobis, *Dokl. Akad. Nauk USSR*, **142**, 105 (1962); **144**, 374 (1962).

Table V. Activation Energies ($E_l - E_T$) and A Factors (A_l/A_T)

$$RH + CH_3\cdot \longrightarrow R\cdot + CH_4 \quad k_l$$

$$PhCH_3 + CH_3\cdot \longrightarrow PhCH_2\cdot + CH_4 \quad k_T$$

Hydrocarbon	Type of C–H[a]	($E_l - E_T$), kcal/mole	A_l/A_T per active H atom
o-Xylene	p	−0.3 ± 0.2	0.8
m-Xylene	p	−0.2 ± 0.2	0.8
p-Xylene	p	−0.3 ± 0.2	0.8
Mesitylene	p	−0.5 ± 0.3	0.5
Ethylbenzene	s	−0.7 ± 0.2	1.5
1,2-Diphenylethane	s	−0.8 ± 0.2	1.3
Indan	s	−1.3 ± 0.4	1.2
Tetralin	s	−2.1 ± 0.3	1.1
Diphenylmethane	s	−1.0 ± 0.4	3.2
Cumene	t	−1.1 ± 0.2	2.7
p-*t*-Butylcumene	t	−1.3 ± 0.3	2.1
Cyclohexylbenzene	t	−1.0 ± 0.2	3.0
Triphenylmethane	t	−2.0 ± 0.7	3.9

[a] p, primary; s, secondary; t, tertiary.

trans- and *cis*-decalin, etc., and a tritiated standard ($C_6H_{11}T$ and (n-$C_3H_7)_2CHT$). Methyl radicals were generated by the decomposition of acetyl peroxide in the range 60–90°.

The radioactivity found in their blanks permitted them to determine the T/H isotope effect for the reaction $RH + CH_3\cdot \rightarrow R\cdot + CH_4$. The results are[8] for $C_6H_{11}T$ (cyclohexane), $A_{Tr}/A_H = 0.58$ and $E_{Tr} - E_H = 2.8$ kcal/mole; and for $(C_3H_7)_2CHT$, A_{Tr}/A_H = ? and $E_{Tr} - E_H = 3.2$ kcal/mole. The agreement with our value $A_{Tr}/A_H \sim 1$ and $E_{Tr} - E_H = 2.7$ kcal/mole is fair.

The Effect of Conformation on the C–H Reactivity. The effect of conformation on the reactivity was discussed by Winstein and Holness[9] who showed that the *observed* rate constant in our case

$$k_{obsd} = (-d[RH]/dt)/[RH][CH_3\cdot]$$

is given by the sum

$$k_{obsd} = \Sigma f_i k_i$$

where f_i denotes the mole fraction of conformer i and k_i its reactivity. Hence, the observed activation energy

$$E_{obsd} = -R d \ln k_{obsd}/d(1/T)$$

is temperature dependent. For example, if the most reactive conformer is energetically unfavorable, $E_{obsd} = E_i + \Delta$, where E_i is the activation energy for a system which contains only the conformer i. This explains the lower activation energy found for indan and tetralin when compared with ethylbenzene or 1,2-diphenylethane. The most reactive conformer of ethylbenzene or 1,2-diphenylethane, possessing the C–H bond perpendicular to the plane of benzene, is energetically less favorable than the one having the C–CH_3 bond perpendicular to the plane of the ring. If E_i denotes the activation energy of the reaction involving the favorable isomer, then $E_{PhCH_2CH_3} = E_i + \Delta$, but $E_{tetralin} \approx E_i$. Hence, the observed activation energy should be higher for ethylbenzene than for tetralin in accord with the data listed in Table V. A similar situation is encountered for cumene; in fact, Δ(cumene) > Δ(ethylbenzene). Thus, the expected decrease in activation energies in the series toluene (primary C–H, Δ = 0), ethylbenzene (secondary C–H, Δ > 0), cumene (tertiary C–H, Δ even greater) should be smaller than that found for the series of aliphatic primary, secondary, and tertiary C–H's. This is shown by our results. On the other hand, the decrease in the observed activation energies of toluene and tetralin (Δ ≈ 0 for both hydrocarbons) should be close to that found in the series of aliphatic hydrocarbons (about 1.7–2 kcal/mole). This is again confirmed by our results.

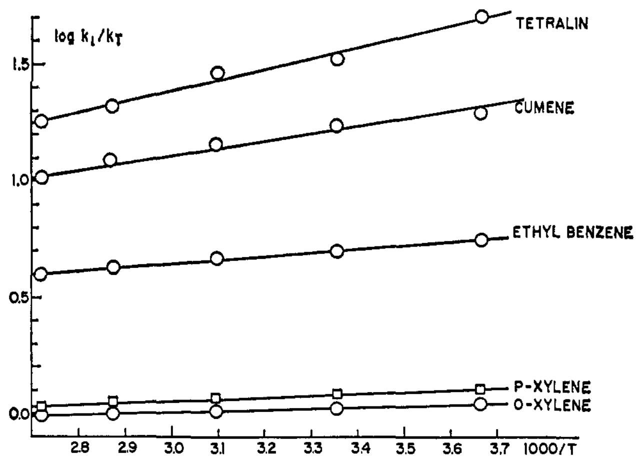

Figure 2.

The temperature dependence of E affects the respective A factors. It is easy to show that A increases as Δ becomes larger. Consequently, the observed changes in A's (see Table V) are accounted for.

General Remarks

From the preceding discussion we may conclude that small differences in the rate constants need not reflect a difference in the intrinsic reactivity of, say, advantageously oriented C–H bonds. For example, they may arise from small differences in Δ. Therefore, the arguments such as advocated by Williams, Oberright, and Brooks,[2] where the increase of k_l for *p*-xylene over *m*-xylene was attributed to hyperconjugation, may be doubtful. Similarly, it is ambiguous to interpret the difference between the k_l values of cumene, *p*-*t*-butylcumene, and cyclohexylbenzene, and it is even more difficult to discuss the small differences in E_l, even if they are free of experimental uncertainty. It is our feeling that the discussion invoking strains in the initial and transition states are of doubtful value when one deals with small variations in k_l or E_l. It is more important to appreciate the constancy of k_l for toluene, the xylenes, and mesitylene, or for ethylbenzene and 1,2-diphenylethane, or for cumene and cyclohexylbenzene. This indicates that basically the reactivity of the C–H bond is determined by it nature: primary, secondary, and tertiary.

Previous studies in this labotatory[10] of competitive radical reactions involving the same reaction center (*e.g.*, CF_3 radical addition to an olefinic, acetylenic, or aromatic center with respect to H abstraction from a hydrocarbon standard) have established that the ratio of A factors is constant. Changes in the reactivity of the

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(8) O. Dobis, Thesis, Moscow University, Moscow, 1962.

(9) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955).

(10) G. E. Owen, Jr., J. M. Pearson, and M. Szwarc, *Trans. Faraday Soc.*, 60, 564 (1964).

substrate are due to changes in the respective activation energies. This present study confirms these findings for a series of competitive reactions involving abstraction of a primary, secondary, or tertiary hydrogen atom from a carbon atom α to an aromatic ring.

Acknowledgment. We wish to thank the Atomic Energy Commission, Division of Research, Contract No. AT(30-1)2728, for financial support of this work. We wish also to thank Dr. Böckman for checking our calculations.

The Effect of Pressure on the *cis–trans* Equilibrium in Poly-L-proline

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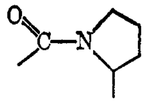
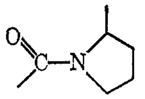
Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, and the Department of Biochemistry and Biophysics, Iowa State University, Ames, Iowa. Received August 7, 1967

Abstract: The effect of pressure on the equilibrium conformation of long-chain poly-L-proline has been studied by means of optical rotation measurements in the solvent acetic acid + 1-propanol (60:40 by volume). A transition from the essentially complete *trans* helix at 1 atm to the complete *cis* helix at 7000 atm was observed, with the midpoint of the transition at 2975 atm. The equilibrium transition curve obeys the equation for the one-dimensional Ising model, taking $\Delta\bar{V}/\sigma^{1/2} = -43.5$ cc/mole, where $\Delta\bar{V}$ is the standard partial molal volume change for the *trans* → *cis* reaction and σ is the interruption constant. The implications regarding the magnitude of σ are discussed, and it is concluded that σ is considerably less than unity, implying a high degree of cooperativity. Molecular models suggest that the cooperative effect originates in positive contributions to the energy of residues at junctions between *cis* and *trans* sequences.

Extensive studies[1] have shown that poly-L-proline exists in solution in two helical forms, usually designated I and II. In form I the peptide units are in the *cis* conformation.[2]



The *cis* helix is right handed and has an axial translation of 1.90 Å per residue. There are 3.3 residues per turn. In form II the peptide units are in the *trans* conformation.[3]



The *trans* helix is left handed, having 3 residues per turn, and has an axial translation of 3.12 Å per residue. The *trans* helix is thus relatively extended, while the *cis* helix is relatively compact.

It was discovered by Gornick, *et al.*,[4] that an equilibrium between the two forms exists in the solvent mixture 1-propanol–acetic acid, and that this equilibrium shifts from one form to the other within a narrow range of solvent composition. The implication of this finding is that the equilibrium is cooperative, *i.e.*, that there is a tendency for peptide units in the same state to group together along the chain. It is desirable to examine this implication in more detail to determine whether the equilibrium behaves according to a reasonable theoretical model, and to characterize the cooperativity in quantitative terms. A satisfactory theory of the dependence of a linear chain equilibrium on solvent composition is lacking at present, and one must look instead to the effects of temperature and pressure for a quantitative study.

We have been attempting to exploit pressure as an environmental variable in the study of cooperative equilibria[5] and were prompted by the above findings to undertake the present study of poly-L-proline. This seemed particularly appropriate in view of the observation of Gornick, *et al.*, that the *cis–trans* equilibrium is practically independent of temperature, implying that the enthalpy difference between the two states is essentially zero. Poly-L-proline proved to be particularly well adapted to a pressure study because the extremely slow approach to equilibrium made possible the determination of its state at high pressures by measurements of optical rotation at atmospheric pressure after removal from the pressure vessel. It was thus possible to attain higher pressures than are presently feasible in an optical rotation cell, and to observe a complete transition between the two helical forms.

Experimental Section

Materials. Poly-L-proline with a nominal molecular weight of 43,000 (DP = 440) was obtained from Mann Research Co. (Lot No. M1251). The specific rotation of this polymer when initially dissolved in acetic acid indicated that it was predominately in the *cis* form. Baker Analyzed Reagent grade acetic acid and 1-propanol were used as solvents.

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(1) Reviewed by E. Katchalski, A. Berger, and J. Kurtz, "Aspects of Protein Structure," G. N. Ramachandran, Ed., Academic Press Inc., New York, N. Y., 1963, p 205.

(2) W. Traub and U. Shmueli, *Nature*, **198**, 1165 (1963).

(3) R. M. Cowan and S. McGavin, *ibid.*, **176**, 1062 (1955).

(4) F. Gornick, L. Mandelkern, A. F. Diorio, and D. E. Roberts, *J. Am. Chem. Soc.*, **86**, 2549 (1964).

(5) J. Rifkind and J. Applequist, *ibid.*, **86**, 4207 (1964).