log $Ze^{1/2}$ (reaction 1) = 11.66, whereas log $Ze^{1/2}$ (reaction 1′) = 11.65.[19] Thus, collision theory does not explain why $A_1 < A_1'$, but the implication is that for reaction 1 there might be more need for orientation in the collision pair. In view of the structural differences between acetone and ethane this conclusion is reasonable.

According to transition-state theory the A factor for a bimolecular reaction is given by (standard state unit concentration)

$$A = (e^2kT/h)\exp[(\Delta S^{\ddagger}_{tr} + \Delta S^{\ddagger}_{rot} + \Delta S^{\ddagger}_{vib})/R]$$

where the $\Delta S^{\ddagger}$'s are the translational, rotational, and vibrational entropies of activation, respectively. The evaluation of the $\Delta S^{\ddagger}$'s for bromine atom reactions has been discussed[19,21] and we have estimated[19] log $A_{1'}$ = 11.7 (T_m = 550°K). Applying the same principles as before, we estimate that log A_1 = 10.9 (550°K), in good agreement with the experimental result. The difference between $A_{1'}$ and A_1 is essentially due to a decrease in $\Delta S^{\ddagger}_{tr} + \Delta S^{\ddagger}_{rot}$ as RH increases in size from C_2H_6 to CH_3COCH_3 without complete compensation by the increase in $\Delta S^{\ddagger}_{vib}$, as is usually the case.[21] Changes in internal rotation make a small contribution to the overall difference at the reaction temperature since the CH_3–CH_3 rotational barrier is 2.9 kcal/mol[16] and the CH_3–$COCH_3$ barrier is 0.8 kcal/mol.[16]

In the above calculations, the two bending and two rocking modes associated with the Br and transferring H atoms were assigned vibrations of ~250 cm^{-1} each. Although the agreement between calculated and experimental A factors is extremely good, these frequencies seem to be too low for what are essentially hydrogen atom motions. Moreover, in the calculations of Fettis, Knox, and Trotman-Dickenson,[21] where the two rocking modes were ignored, the bending frequencies were assigned extremely low values of <100 cm^{-1}. Of course, all of these calculations are based on a linear[22] configuration for C–H–Br in the transition-state complex. However, should the configuration be bent then major contributions to $\Delta S^{\ddagger}_{vib}$ would be due to internal rotations of R in the R–H–Br complex and the bending modes may be assigned much higher frequencies.

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Kinetics of Hydrogen–Deuterium Exchange in Poly(N-vinylacetamide) Measured by Infrared Spectroscopy

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Abstract: The hydrogen–deuterium exchange in D_2O solutions of poly(N-vinylacetamide) has been studied as a function of pD at four temperatures. The rate constants observed for the exchange of the hydrogen atoms of the amide groups of the polymer are lower by a factor of ~20 than the corresponding exchange rate constants of N-methylacetamide. The interpretation of this observation is discussed and, as a likely explanation of the result, it is suggested that fast fluctuations of the conformation of the dissolved polymer molecules occur, and that the amide groups of the polymer are protected from solvent exposure for about 95% of the time.

Hydrogen atoms attached to electronegative atoms in groups such as –COOH, $-NH_2$, –OH, –SH, and –CONH– are known to be labile; when compounds containing such groups are dissolved in water, an exchange of hydrogen atoms takes place between the groups and the solvent. Measurements of the rate of this exchange in aqueous protein solutions are being used as a tool in studies of protein conformations.[2,3] It is quite generally observed that part of the hydrogen atoms in protein molecules exchanges with those of solvent water at considerably slower rates than do corresponding hydrogen atoms in low molecular weight compounds or in randomly coiled polypeptides.

It has been a basic assumption, underlying many studies of the hydrogen exchange, that this reduced reactivity of hydrogen atoms in protein molecules is characteristic of the conformation of the proteins, and, therefore, that measurements of the exchange rates may contribute to the elucidation of the nature of protein conformations. It was, however, pointed out by Klotz and coworkers,[2b,4,5] and also discussed in ref 2a, that a slow exchange in aqueous solutions might be explained partly or entirely by a change in the structure of the water surrounding the dissolved molecules, and that a more extensive investigation of the exchange in solutions of molecules simpler than proteins is needed before any definite conclusions can be drawn about the interpretation of the slow exchange in protein

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(1) Israel Institute for Biological Research, Ness-Ziona, Israel.

(2) (a) Aa. Hvidt and S. O. Nielsen, *Advan. Protein Chem.*, **21**, 287 (1966); (b) I. M. Klotz, *J. Colloid Interface Sci.*, **27**, 804 (1968).

(3) F. S. Parker and K. R. Bhaskar, *Appl. Spectrosc. Rev.*, **3**, 91 (1969).

(4) H. Leichtling and I. M. Klotz, *Biochemistry*, **5**, 4026 (1966).

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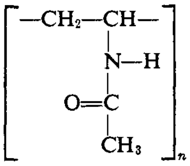
solutions. Scarpa, Mueller, and Klotz[5] recently found that the amide groups of the polymer poly(N-isopropylacrylamide) in D_2O solutions exchange their hydrogen atoms at rates which are slower by a factor of ~50 than the exchange rates of the amide hydrogen atom of N-isopropylpropionamide, the monomeric analog of the repeating unit of the polymer. Following this line of reasoning, we have measured the exchange rates of amide hydrogen atoms in D_2O solutions of the polymer poly(N-vinylacetamide)



$$\left[-CH_2-CH(-NH-C(=O)-CH_3)-\right]_n$$

and found that the exchange rates are slower by a factor of ~20 than the exchange rates in solutions of N-methylacetamide, the monomeric analog of the side-chain groups of the polymer. The interpretation of these observations is discussed below.

Experimental Section

Chemicals. D_2O was purchased from Norsk Hydro, Norway, and was warranted to be 99.7% D_2O. DCl was obtained from Fluka as a 38% solution of DCl in D_2O. Polyvinylphthalimide was a product of Monomer-Polymer Laboratories, Catalog No. 8171. All other reagents and solvents used were standard laboratory grade.

Instrumental. Viscosities were measured with viscometers of the Ubbelohde type. Flow times were measured by viscometer reader VR-U, available from Rehovoth Instruments Ltd., Israel. The flow times of water were approximately 100 sec. A Mechrolab osmometer, Model 503, was used for measurements of osmotic pressure. Membranes used were Sartorius Ultrafilter 12136 (cellulose nitrate). A radiometer pH meter, Model TTT1c, furnished with a combined microelectrode, G2221c, served for measurements of pH. Infrared absorption of the polymer in D_2O was measured with a Beckman IR 9 spectrophotometer used in double-beam operation with solvent in the reference beam. The optical cells had CaF_2 windows; the optical path length was 0.1 mm. Water circulating in jackets around the cells permitted adjustment of the cell temperature; the temperature of the solution within the cells was measured by means of a thermocouple placed directly in the liquid.

Preparation and Characterization of the Polymer. Poly(N-vinylacetamide) was prepared from polyvinylphthalimide by the method of Reynolds and Kenyon.[6] Polyvinylphthalimide (10 g) was refluxed with 15 ml of 100% hydrazine hydrate and 3.5 ml of water for 26 hr, by which time dissolution was complete. The viscous yellowish solution was poured into 500 ml of ethanol, and the precipitate was leached several times with fresh portions of ethanol and dried in a vacuum oven at 50°. The yield of the phthalylhydrazide salt of polyvinylamine was 7.7 g. This salt was then refluxed for 1.5 hr with 20 ml of acetic anhydride, cooled, and poured into 300 ml of acetone. The precipitated poly(N-vinylacetamide) was purified by repeated precipitation from an aqueous solution by a large excess of acetone; it was then lyophilized from an aqueous solution, and finally refluxed for 2 hr with acetone to remove the last traces of low molecular weight compounds and vacuum dried. The yield was 3.6 g of a fluffy, slightly yellowish polymer.

Anal. Calcd for C_4H_7NO: C, 56.45; H, 8.29; N, 16.46. Calcd for $C_4H_7NO\cdot H_2O$: C, 46.59; H, 8.80; N, 13.58. Found: C, 46.53; H, 7.55; N, 13.32.

On the basis of the analysis it seems reasonable to assume that one molecule of water per repeat unit was not removed by the drying procedure employed.

The polymer did not contain any residual phthalimide groups, as seen from the uv spectrum, where no peaks could be detected at 240 mμ. The intrinsic viscosity in aqueous solution at 25° was 1.15 dl/g. Osmotic pressure measurements in water at 25° indicate a molecular weight of 44,000 (degree of polymerization about 500).

The Hydrogen-Deuterium Exchange Method. The rate of hydrogen exchange was measured by a modification of the infrared spectrophotometric method, originally suggested by Blout, *et al.*[7] The experimental procedure is briefly described in the following; for further details the reader is referred to ref 2a or 3. The exchange reaction

$$\text{-CONH-} + D_2O \longrightarrow \text{-COND-} + HOD \qquad (1)$$

can be followed spectrophotometrically by measurements of the disappearing amide II absorption band due to -CONH- groups. For solutions of poly(N-vinylacetamide) in D_2O the maximum of the amide II band was found at 1573 cm^{-1} (see Figure 1).

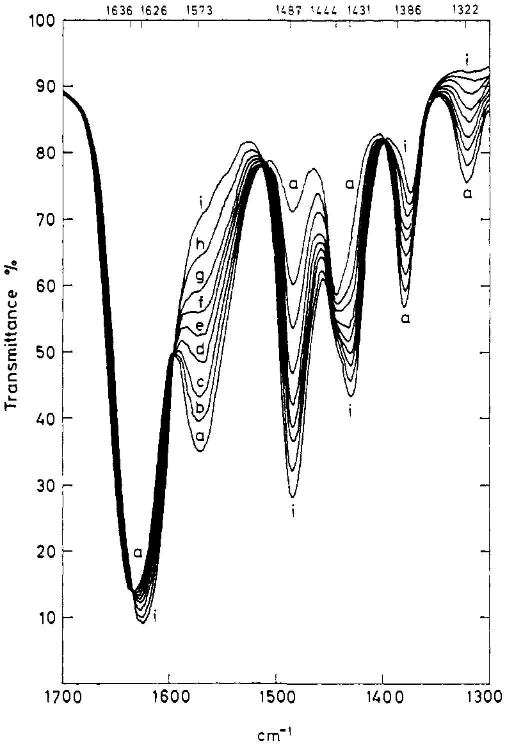


Figure 1. The infrared spectrum of poly(N-vinylacetamide) in D_2O, pD 5.6, 10°, recorded in the region 1300–1700 cm^{-1} at: a, 15 min; b, 44 min; c, 72 min; d, 114 min; e, 156 min; f, 197 min; g, 253 min; h, 332 min; and i, 731 min after dissolution. (Scanning of a spectrum takes about 10 min, and the times given refer to the recording of the amide II band at 1573 cm^{-1}.)

An exchange experiment was initiated by the addition of 0.5 ml of D_2O to a sample of about 10 mg of the polymer, lyophilized from a 2% solution in ordinary water. The D_2O was buffered with DCl or 0.01–0.1 *M* sodium acetate; pH was measured on the polymer solution and converted to pD by means of the formula pD = pH + 0.40.[8,9] The polymer was dissolved at the temperature of the exchange experiment, and the solution was then transferred to the optical cell which was placed in the photometer,; the transmittance at 1573 cm^{-1} was recorded as a function of time. At suitable intervals the region 1300–1700 cm^{-1} was scanned.

The pseudo-first-order exchange rate constant k of reaction 1 was calculated from graphs of log $(OD_t - OD_\infty)$ *vs.* t. Figure 2 shows such a graph for poly(N-vinylacetamide) in D_2O at 20° and pD 4.2. OD_t is the absorption at 1573 cm^{-1} at time t, and OD_∞ is the absorption at the same frequency after completion of the exchange, *i.e.*, after at least eight half-lives at the temperature of the experiment, or after heating the solution to 40° for 1 hr. $(OD_t - OD_\infty)$ is considered to be proportional to the concentration of

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[6] D. D. Reynolds and W. O. Kenyon, *J. Amer. Chem. Soc.*, **79**, 911 (1947).

[7] E. R. Blout, C. De Loze, and A. Asadourian, *ibid.*, **83**, 1895 (1961).

[8] K. Mikkelsen and S. O. Nielsen, *J. Phys. Chem.*, **64**, 632 (1960).

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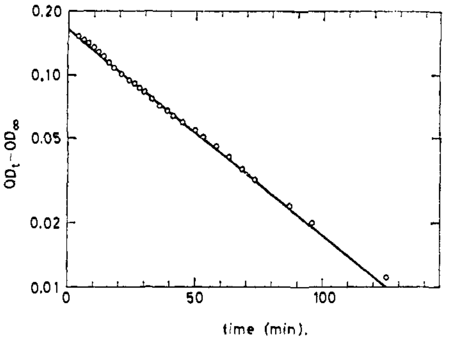

Figure 2. Semilogarithmic plot of the amide II absorption as a function of time for poly(N-vinylacetamide) in D_2O, pD 4.2, 20°.

unexchanged -CONH- groups, so the slope of the straight line on Figure 2 determines the exchange rate constant k.

Considering Figure 1, which shows the infrared absorption of poly(N-vinylacetamide) in D_2O at various degrees of exchange, it might be tempting to measure the exchange by the absorption at the maximum frequency of one of the changing absorption bands in the region 1300–1500 cm^{-1}. Such measurements, however, would be hampered by a broad HOD absorption in this region.

Results

Infrared Spectra. Figure 1 shows the infrared spectrum in the region 1300–1700 cm^{-1} of poly(N-vinylacetamide) in D_2O, at 10° and pD 5.6, recorded at various times after dissolution of the polymer, *i.e.*, at various degrees of H–D exchange in the amide groups. It appears from the figure that the exchange is accompanied by extensive changes in the infrared spectrum.

The three amide bands, the so-called amide I, II, and II bands, typical of the absorption of -CONH- groups in this region, were found at 1636, 1573, and 1322 cm^{-1}, respectively. These bands are due to vibrations of the -CONH- group and all undergo changes on deuteration. The amide I band is mainly associated with a CO stretching,[10] and on deuteration of the amide group the frequency of the maximum of this absorption was displaced to 1626 cm^{-1} and an increase of the extinction coefficient was observed. According to Fraser and Price,[11] the amide II and amide III bands arise from interaction between the symmetrical stretching mode of the O=CN group and the NH in-plane bending mode. On deuteration of the amide group these bands disappear; the appearing absorption at 1487 cm^{-1} is the -COND- analog of the amide II band, commonly found at a frequency about 100 cm^{-1} below the frequency of the amide II absorption.[2a]

The internal bending modes of the methyl group are expected to have frequencies in the range 1300–1500 cm^{-1}. The absorption observed at 1444 cm^{-1} remained uninfluenced by the exchange, and is most likely due to a CH_3-C bending frequency.[12] The sensitivity to H–D exchange of the absorption at 1431 cm^{-1} (appearing) and at 1386 cm^{-1} (disappearing) supports the assumption made by Bradbury and Elliott,[13] for presumably corresponding bands in spectra of N-methylacetamide, that these bands cannot be ascribed to simple vibrations of the methyl groups.

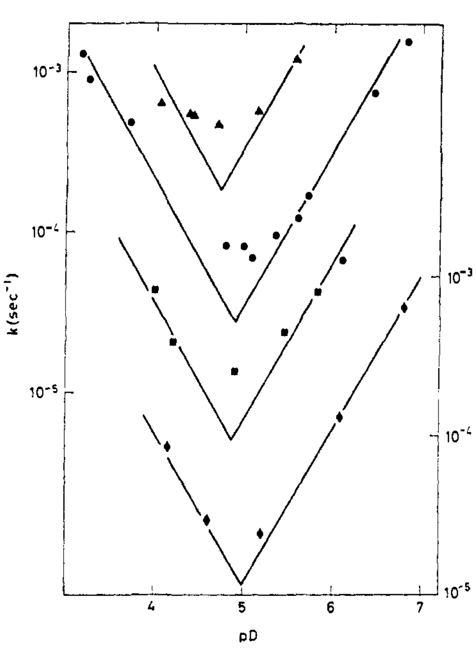

Figure 3. Semilogarithmic plot of the measured exchange rate constants, k, of poly(N-vinylacetamide) as a function of pD: ▲, at 25°; ■, at 20°; ●, at 10°; and ◆, at 4°. The left-hand scale refers to the two upper curves, the right-hand scale to the two lower ones.

Kinetic Data. All measurements of exchange rates were made in solutions of poly(N-vinylacetamide) in D_2O so dilute ([-CONH-] < 0.1 M) that for all practical purpose the back-reaction in the equilibrium

$$\text{-CONH-} + D_2O \rightleftharpoons \text{-COND-} + HOD \qquad (2)$$

could be neglected and the concentration of D_2O considered to be independent of the degree of exchange. The exchange rates measured are, therefore, rates of the forward reaction of the equilibrium 2, normally proceeding as a pseudo-first-order reaction.

The exchange was studied at four temperatures, 4, 10, 20, and 25°, and the first-order rate constants, k, measured are summarized in Figure 3 as a plot of log k *vs.* pD. The straight lines on this figure are drawn with the slopes $d \log k/dpD = \pm 1$ (see later).

At 4° and pD <4.1, the exchange rate curves were found to deviate from first-order kinetics. Plots of log ($OD_t - OD_\infty$) showed an upward curvature, and the initial slope was considerably steeper than expected for this temperature. We do not know of any explanation for this phenomenon, but it might be recalled that the temperature of these experiments is only slightly above the freezing point of D_2O at 3.92°, so ice-like structures may be formed in the solvent water, complicating the kinetics of the exchange reaction.

Discussion

As pointed out by Morawetz,[14] the slow rate of hydrogen exchange in aqueous solutions of macromolecules is a notable exception to the more general rule that functional groups attached to polymer molecules

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[10] T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

[11] R. D. B. Fraser and W. C. Price, *Nature (London)*, **170**, 490 (1952).

[12] B. Schneider, A. Horeni, H. Pivcova, and J. Honzl, *Coll. Czech. Chem. Commun.*, **30**, 2196 (1965).

[13] E. M. Bradbury and A. Elliott, *Spectrochim. Acta*, **19**, 995 (1963).

[14] H. Morawetz, "Macromolecules in Solution," Interscience, New York, N. Y., 1965, Chapter 9.

have reactivities similar to those of the same groups in small molecules. Several interesting examples of exceptional reactivities are mentioned in ref 14, and among the reactions discussed the H-D exchange is advantageous because it causes only minor structural changes in the molecules involved.

Before discussing the interpretation of the measured exchange rates in solutions of poly(N-vinylacetamide), we shall summarize briefly what is known about the exchange of amide hydrogen atoms in solutions of small molecules.[15-19]

In dilute solutions of low molecular weight peptides and amides in D_2O the forward reaction of equilibrium 2 proceeds as a pseudo-first-order reaction

$$\frac{d}{dt}[\text{-CONH-}] = -k[\text{-CONH-}]$$

The exchange is catalyzed by D_3O^+ and by OD^- ions, and the first-order rate constants, k, observed can be expressed as

$$k = k_{D_2O} + k_{D_3O^+}[D_3O^+] + k_{OD^-}[OD^-]$$

In purely aqueous solutions k_{D_2O}, the contribution to k from the uncatalyzed reaction, is generally negligible, so that

$$k \approx k_{D_3O^+}[D_3O^+] + k_{OD^-}[OD^-] \tag{3}$$

The minimal value of k, $k_{\min}$, and the value of pD, $\text{pD}_{\min}$, for which $k = k_{\min}$, are given by the expressions[4]

$$\begin{aligned} k_{\min} &= 2(K_W k_{D_3O^+} k_{OD^-})^{1/2} \\ \text{pD}_{\min} &= -\frac{1}{2}\log\,(K_W k_{OD^-}/k_{D_3O^+}) \end{aligned} \tag{4}$$

where K_W is the dissociation constant of D_2O; $K_W = [D_3O^+][OD^-]$. From eq 4 one gets

$$\begin{aligned} k_{D_3O^+} &= \frac{1}{2}k_{\min}10^{\text{pD}_{\min}} \\ k_{OD^-} &= \frac{1}{2}k_{\min}10^{\text{p}K_W - \text{pD}_{\min}} \end{aligned} \tag{5}$$

which, introduced into eq 3, leads to the expression

$$k \approx \frac{1}{2}k_{\min}(10^{\text{pD}-\text{pD}_{\min}} + 10^{\text{pD}_{\min}-\text{pD}}) \tag{6}$$

The pD dependence of the exchange rate constant k can thus be characterized by the parameters $k_{\min}$, $\text{pD}_{\min}$ as well as by $k_{D_3O^+}$, k_{OD^-}.

The advantage of using the parameter $k_{\min}$ in discussions of exchange rates in solutions of macromolecules has been explained by Leichtling and Klotz.[4] These authors pointed out that comparisons between exchange rates of various compounds measured at some given value of pD may not be very meaningful if the compounds compared have different values of $\text{pD}_{\min}$. Comparison of a number of small molecules proved that, whereas the observed values of $\text{pD}_{\min}$ are strongly influenced by the electron-withdrawing effect of substituents near the exchanging amide groups, the values of $k_{\min}$ at a given temperature are strikingly similar. In other words, in eq 4, the inductive effects of substituents on the amide group may influence the ratio $k_{OD^-}/k_{D_3O^+}$, but do not change the product $k_{D_3O^+}k_{OD^-}$. It is therefore meaningful to talk about values of $k_{\min}$ typical for the exchange rates of amide hydrogen atoms in solutions of low molecular weight compounds. Although $k_{\min}$ is sensitive to steric effects,[17] it is, for small molecules in which the amide groups are presumably freely exposed to solvent water, of the order of 10^{-3}–10^{-2} sec^{-1} at room temperature.

Table I summarizes values of $k_{\min}$ and $\text{pD}_{\min}$ for isopropylpropionamide, poly(N-isopropylacrylamide), N-methylacetamide, and poly(N-vinylacetamide). The measured values of $k_{\min}$ for each polymer are seen to be lower than those for the corresponding monomer; the values of $k_{\min}$ for poly(N-vinylacetamide) are smaller by a factor of ~20 than corresponding values for N-methylacetamide. Viscosity measurements indicate a random coil conformation for both polymers.

Table I. Exchange Rate Parameters for Polymers and Monomers

	Temp, °C	$k_{\min}$, sec^{-1}	$\text{pD}_{\min}$
Isopropylpropionamide	25[a]	2.5×10^{-3}	5.38
Poly(isopropylacrylamide)	25[a]	5.0×10^{-5}	5.0
N-Methylacetamide	25[b]	8.3×10^{-3}	5.5
	24[c]	7×10^{-3}	5.45
	15[b]	3.3×10^{-3}	5.5
	12[c]	10^{-3}	5.5
Poly(N-vinylacetamide)	25[d]	4×10^{-4}	4.8
	20[d]	2×10^{-4}	4.9
	10[d]	5×10^{-6}	4.9
	4[d]	2×10^{-5}	5.0

[a] Reference 5. [b] Reference 19. [c] Reference 17, Figure 8. [d] This work.

It has been suggested[2b,4,5] that the slow exchange rates generally observed in solutions of macromolecules could be explained, at least partly, by assuming that water in the immediate environment of a macromolecule has a different structure from normal water and a lower dissociation constant. It appears from eq 4 and 6 that low values of the rate constants k and $k_{\min}$ could, in principle, be explained by assuming low values of K_W. It should, however, be noted that K_W entering eq 4 is the dissociation constant of water in the phase of the solution in which pH has been measured, *i.e.*, in the bulk phase. In order to explain the fact that the exchange rates in solutions of poly(N-vinylacetamide) are slower by a factor of ~20 than in solutions of N-methylacetamide, we would have to make the rather unlikely assumption that K_W in the bulk phase of the polymer solution is smaller by a factor of 400 than in solutions of the monomer. Furthermore, according to eq 4, low values of K_W should be associated with high values of $\text{pD}_{\min}$, but the small shift observed in $\text{pD}_{\min}$ for the polymer solutions, as compared to solutions of the monomers, is toward lower, instead of higher, values.

Available data on hydrogen exchange neither confirm nor disprove the possibility that the character of water in the environment of a macromolecule is different from that of normal water. The slow exchange

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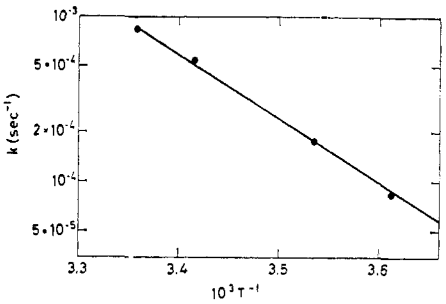

Figure 4. Semilogarithmic plot of the exchange rate constant of poly(N-vinylacetamide) at pD 4.1 as a function of reciprocal temperature.

rates could, however, be explained by assuming that the local concentration of water (and therefore of D_3O^+ and OD^-) in the environment of the amide group is lower, on the average, in solutions of macromolecules than in solutions of low molecular weight compounds. We tentatively suggest that the exchange rates be explained in terms of the reaction mechanism originally suggested for the exchange of hydrogen atoms in protein molecules.[2a,20] This mechanism assumes that a macromolecule in solution undergoes statistical fluctuations, changing with time the relative positions of its constituent groups, *i.e.*, changing conformation. In some conformations a given amide group is freely exposed to the solvent, and the rate constant of exchange of its hydrogen atom is similar to that of an amide group in a corresponding low molecular weight compound. In other conformations the group considered is protected by other parts of the macromolecule from exposure to the solvent, and, therefore, prevented from exchanging its hydrogen atom. According to this mechanism the ratio $k_{\text{polymer}}/k_{\text{monomer}}$ is a measure of the fraction of time spent, on the average, by the amide groups of the polymer in free contact with the solvent. It is a consequence of this mechanism that the activation energy of the exchange reaction is similar for a polymer and for the corresponding monomer. Figure 4 shows an Arrhenius plot of the rate constants measured for poly(N-vinylacetamide) at pD 4.1. The straight line drawn corresponds to an activation energy for the acid-catalyzed reaction of 18 kcal/mol, in satisfactory agreement with the value of 17 kcal/mol reported by Klotz and Frank[18] for the corresponding reaction of N-methylacetamide.

We take this study of the H–D exchange in solutions of poly(N-vinylacetamide) as supporting the idea that kinetic investigations of the hydrogen exchange in macromolecular solutions may offer information about the accessibility of the amide groups of the macromolecules to the solvent, or about the extent to which the macromolecules are "freely drained." The data presented in Table I suggest that the amide groups of poly(N-vinylacetamide) spend about 5% of the time exposed to the solvent. The inaccessibility of the amide groups to the solvent need not result from the overall conformation of the macromolecule, but may be an effect of interactions among neighboring groups.

Acknowledgments. One of the authors (Aa. H.) wishes to thank the Carlsberg Foundation for grants for experimental equipment used in this investigation. The skilled technical assistance of Mrs. Gerda Christensen is gratefully acknowledged.

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Nonplanarity in Hexafluorobutadiene as Revealed by Photoelectron and Optical Spectroscopy

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Abstract: Comparison of the photoelectron spectra of the perfluorinated diene $F_2C{=}CF{-}CF{=}CF_2$ and its hydrogen analog, butadiene, demonstrates that the interaction between the two ethylenic groups in the former is only one-third that in the latter, whereas in $F_2C{=}CH{-}CH{=}CF_2$, the full interaction is observed. On this basis it is suggested that the carbon skeleton of hexafluorobutadiene is nonplanar. In support of this, the optical spectra of butadiene and 1,1,4,4-tetrafluorobutadiene are of the usual sort, each with a very strong $N \rightarrow V_1$, but very weak $N \rightarrow V_2$ transition. The $N \rightarrow V_2$ transition in hexafluorobutadiene, however, is the stronger of the two, and it is concluded on the basis of a simple intramolecular exciton calculation that the observed $(N \rightarrow V_1)/(N \rightarrow V_2)$ intensity ratio is consistent with a cisoid molecular structure, the dihedral angle being 42 ± 15°, in agreement with a subsequent electron diffraction value of 47.60 ± 0.58°.

Questions regarding the conformations about the single and double bonds of substituted 1,3 dienes are of increasing interest, as modern experimental methods put the answers more and more within reach. In this paper, we report the results of an investigation of the optical and photoelectron spectra of hexafluorobutadiene, directed toward determining its conformation in the gas phase. For comparison, the molecules butadiene and 1,1,4,4-tetrafluorobutadiene, both of known conformation, were also investigated.

Butadiene itself exists in the *trans*-planar configuration in the gas phase, possibly in equilibrium with a