Kinetic Studies on the Influence of Conformation and Chain Length on the Reaction of Hydroxy Radicals with Poly(acrylic acid) in Solution

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ABSTRACT: The rate constant of the reaction of OH radicals with sodium poly(acrylate) $k_{\mathrm{OH+NaPAA}}{}^{\mathrm{M}}$ in aqueous solution at room temperature has been measured using the pulse radiolysis technique and applying competition kinetics (standard scavengers: *p*-nitrosodimethylaniline and KSCN). $k_{\mathrm{OH+NaPAA}}{}^{\mathrm{M}}$ depends on the chain length *n* according to $k_{\mathrm{OH+NaPAA}}{}^{\mathrm{M}} \propto n^{0.80}$. Such a dependence is expected for a rodlike conformation of the macromolecules. The conformation dependence of the reaction was demonstrated by measuring $k_{\mathrm{OH+NaPAA}}{}^{\mathrm{M}}$ as a function of pH and in the presence of added salt. With increasing pH $k_{\mathrm{OH+PAA}}$ increases but does not level off as chain expansion does. The additional increase at pH >6 probably reflects reactivity differences between the undissociated and the dissociated forms of the macromolecules. The observed salt effect parallels fairly well experimental and theoretical findings on the dependence of conformation on salt concentration.

Previous experiments[2a] concerning the reaction of OH radicals with poly(ethylene oxide) (PEO), poly(vinylpyrrolidone) (PVP), and dextran in aqueous solution have shown that the following relation holds between the bimolecular rate constant $k_{\mathrm{OH+PH}}{}^{\mathrm{M}}$ (l. mol^{-1} sec^{-1})[3] and the number-average degree of polymerization *n*

$$k_{\mathrm{OH+PH}}{}^{\mathrm{M}} \propto n^{x} \qquad (1)$$

(If $k_{\mathrm{OH+PH}}$ is expressed in l. base mol^{-1} sec^{-1} this relation corresponds to $k_{\mathrm{OH+PH}}{}^{\mathrm{m}} \propto n^{x-1}$.)

It was demonstrated that *x* is equal to $(a + 1)/3$, where *a* is the exponent in the relationship $[\eta] = KM^{a}$. This behavior is expected for linear polymers forming coils in solution and consisting of base units whose reactivity toward OH radicals is very high, *i.e.*, the partial reactivity per base unit corresponds to the order of magnitude of encounter-controlled processes. In such a case an OH radical penetrating a coil will already react with a very high probability in the outer part of the coil thus reducing the average partial reactivity per base unit. Experimentally this behavior was evidenced with coiled polymers in aqueous solution. As expected, the exponent *x* was found to be equal to 0.55–0.57.

In order to substantiate the influence of conformation on fast reactions in the encounter-controlled regime we extended the investigations to polyelectrolytes whose conformation may easily be changed by varying the degree of neutralization or adding low molecular weight electrolytes.

In the following experiments are described which were carried out to measure the rate constant of the reaction of OH radicals with poly(acrylic acid) as a function of chain length, pH, and concentration of added sodium perchlorate.

Experimental Section

Preparation and Characterization of Polymers. The poly(acrylic acid) samples used during this work are listed in Table I. PAA-1 was a sample kindly supplied by Professor R. C. Schulz. The samples PAA-2 to PAA-4 were obtained by polymerizing acrylic acid in aqueous solution using $K_2S_2O_8$ as an initiator. All samples were reprecipitated several times as sodium salts from aqueous solutions with ethanol at a polymer concentration of 1 wt %. Aqueous solutions of the salts were dialyzed for at least 2 weeks. Weight-average molecular weights of the PAA samples were determined by the light-scattering method using a Sofica instrument in 0.1 *N* NaCl.

Determination of Rate Constants. OH radicals were generated by pulse irradiating aqueous polymer solutions with 1.5-meV electrons using a van de Graaff generator (pulse duration 1 μsec, pulse dose *ca.* 250 rad). The polymer concentration amounted to 10^{-3} base mol l.$^{-1}$.

For the determination of rate constants, $k_{\mathrm{OH+PH}}$, competition kinetics were applied using *p*-nitrosodimethylaniline (PNDA) and KSCN as scavengers ($k_{\mathrm{OH+PNDA}} = 1.3 \times 10^{10}$ l. mol^{-1} sec^{-1}; $k_{\mathrm{OH+SCN^-}} = 1.1 \times 10^{10}$ l. mol^{-1} sec^{-1}). In order to scavenge H and $e_{\mathrm{aq}}{}^{-}$ the solutions were saturated with O_2. Optical densities of the solutions were measured immediately after the microsecond pulse. From the ratio of optical densities $\Delta E_0/\Delta E$ obtained for various ratios of the concentration of polymer and scavenger [PH]/[S], the rate constant $k_{\mathrm{OH+PH}}$ was calculated according to

$$\Delta E_0/\Delta E = 1 + (k_{\mathrm{OH+PH}}[\mathrm{PH}]/k_{\mathrm{OH+S}}[\mathrm{S}]) \qquad (2)$$

The subscript 0 denotes the absence of polymer. Typical plots according to eq 2 are shown in Figure 1.

Results and Discussion

OH + NaPAA, Chain Length Dependence of the Rate Constant. Figure 2 shows the chain-length dependence of the rate constant $k_{\mathrm{OH+PH}}{}^{\mathrm{M}}$ for sodium polyacrylate (curve b). For comparison curve c of Figure 2 shows the values obtained with PVP and PEO during previous work.[2a] It is easily recognized that $k_{\mathrm{OH+PH}}$ increases more strongly with *n* in the case of NaPAA than for nonelectrolyte polymers. In addition, the values obtained at constant *n* are higher in the case of NaPAA. We think that the different behavior reflects differences in conformation. Whereas PVP and PEO are rather tightly coiled, NaPAA is certainly highly extended due to Coulombic repulsion. It has been reported that in the case of sodium polymethacrylate[4] and of sodium polyphosphate[5,6] the polyions are fully extended and have the shape of rods in the complete absence of added salt. Sodium polyacrylate should behave the same way.

In Figure 3 the data of Figure 2 are represented in terms of $k_{\mathrm{OH+PH}}{}^{\mathrm{m}} = f(n)$. It is seen, on the one hand, that the rate constant only slightly decreases with increasing *n* in the case of NaPAA. On the other hand, the decrease is much more strongly pronounced in the case of PVP and

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(1) National Iranian Steel Corp., Ariamehr Steel Plant, Esfahan, Iran.

(2) (a) A. Behzadi, U. Borgwardt, A. Henglein, E. Schamberg, and W. Schnabel, *Ber. Bunsenges. Phys. Chem.*, 74, 649 (1970); (b) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. B*, 742 (1966).

(3) PH designates a macromolecule which undergoes H-atom abstraction by the reaction: $\mathrm{OH + PH \rightarrow H_2O + P}$.

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Table I
Poly(acrylic acid) Samples Used During This Work and the Rate Constant of the Reaction of the Corresponding Sodium Salts with OH Radicals

Polymer	$\bar{n}_w$[a]	$k_{OH+PH}{}^m$ (l. base mol^{-1} sec^{-1})	$k_{OH+PH}{}^M$[b] (l. mol^{-1} sec^{-1})
PAA-1	9.0×10^3	3.5×10^8	1.4×10^{12}
PAA-2	1.3×10^3	3.2×10^8	2.1×10^{11}
PAA-3	5.8×10^2	4.0×10^8	1.2×10^{11}
PAA-4	3.2×10^2	4.5×10^8	7.0×10^{10}

[a] Weight-average degree of polymerization. [b] Calculated by assuming that $(\bar{n}_w/\bar{n}_n) = 2.0$.

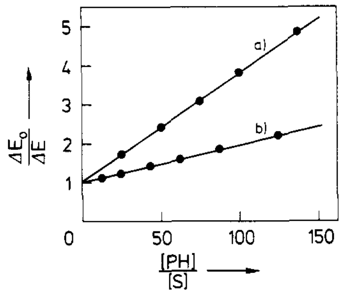
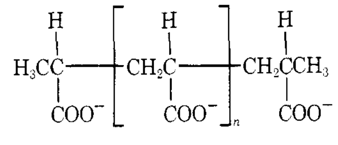


Figure 1. Typical plot of $\Delta E_0/\Delta E$ *vs.* [PH]/[S] for the determination of the rate constants $k_{OH+PH}{}^m$ according to eq 2: (a) NaPAA (10^{-3} base mol. l.$^{-1}$), $\bar{n}_w = 9 \times 10^3$, pH 8.2, scavenger PNDA; (b) PAA (10^{-3} base mol. l.$^{-1}$), $\bar{n}_w = 9 \times 10^3$, pH 1.3 ($HClO_4$ added), scavenger KSCN.

PEO. Since the rate constant expresses a reaction probability, this graph demonstrates that the probability for an OH attack of a base unit of NaPAA is much higher than for a base unit of the tightly coiled polymers. However, the polymeric character still prevails upon the kinetics of the reaction OH + NaPAA as may be shown by a comparison with low molecular weight compounds. Anbar *et al.*[2b] have investigated the kinetics of the reaction of OH radicals with a great number of low molecular weight aliphatic carboxylate ions and have found that the rate constants for the OH attack can be obtained by the summation of the contributions of partial reactivities of H atoms at different positions of the molecule. With the partial reactivity values given by those authors[2b] one finds for a polyion of the structure



$$\mathrm{H_3C\overset{H}{\underset{COO^-}{C}}-\left[CH_2\overset{H}{\underset{COO^-}{C}}\right]_n-CH_2\overset{H}{\underset{COO^-}{C}}CH_3}$$

that the rate constant amounts to

$$k_{OH+PH}{}^M = (1.9 + 1.13n)10^9 \text{ l. mol}^{-1} \text{ sec}^{-1} \qquad (3)$$

According to eq 3 $k_{OH+PH}{}^M$ should be proportional to $n^{1.0}$ for sufficiently high values of n. Curve a in Figure 2 was calculated according to eq 3. The experimental curve lies significantly below the calculated one. It should be pointed out that the application of eq 3 implies a state of complete neutralization of the polyacrylate chain which is achieved by the neutralization of low molecular weight aliphatic carboxylic acids. With polyacids a different kinetic situation may be encountered because counterion condensation[7,8a] takes place. It has been reported[8b,9] that the fraction of condensed counterions amounts to 0.65 for fully neutralized poly(acrylic acid) ($\alpha = 1$). Furthermore it was claimed[8b] that condensed counterions at least partially penetrate the hydration layer around the polyion. Thereby it becomes feasible that the partial reactivity of H atoms in α position to carboxylate groups may be lowered, which finally results in experimental values smaller than those calculated according to eq 3 and plotted as curve a in Figure 2.

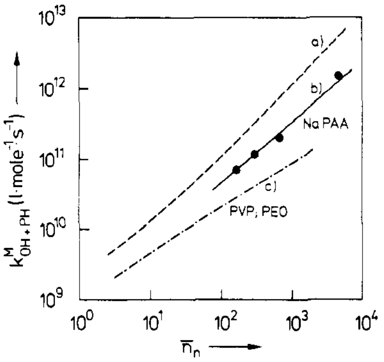


Figure 2. $k_{OH+PH}{}^M$ as a function of chain length. Curve a calculated according to eq 3. Curve b calculated according to eq 4 and experimental values obtained with sodium polyacrylate. Curve c experimental values obtained with poly(vinylpyrrolidone) and poly(ethylene oxide).

The data of Figure 2 may also be brought in comparison with the theory of diffusion-controlled reactions based on Smoluchowski's equation. It has been shown[2a] that such a treatment of data explains the almost square-root dependence of $k_{OH+PH}{}^M$ on n in the case of coil-shaped polymers. Braams and Ebert[10] proposed that the collision frequency Σ of small particles diffusing into a void space of the form of a long cylinder of length L and radius of rotation r can be expressed as

$$\Sigma = 2\pi DN10^{-3}\frac{L}{\ln(L/r)} \text{ l. mol}^{-1} \text{ sec}^{-1} \qquad (4)$$

D denotes the sum of the diffusion coefficients of the reactants and N Avogadro's number. By setting $\Sigma = k_{OH+PH}{}^M$ and taking $L = 4.1 \times 10^{-8}\ n$ cm, $r = 3 \times 10^{-8}$ cm and $D_{OH} = 2 \times 10^{-5}$ cm^2 sec^{-1} values of $k_{OH+PH}{}^M$ were calculated. The results are presented by the full line (b) in Figure 2 with a slope of about 0.80. It is seen that the experimental values fit fairly well on this straight line.

OH + NaPAA, pH Dependence of the Rate Constant. Following the concept of conformation dependence of k_{OH+PH} one expects a rather strong pH effect. From the previous work[4,11-16] on synthetic polyacids based mainly on viscosimetric investigations it is well known that polyacids at low pH, *i.e.*, in the undissociated state, form highly coiled molecules. By increasing the pH, *i.e.*, by ionizing the carboxylic acid groups the macromolecules unfold and assume highly extended conformations at large degrees of dissociation. Evidence for this behavior was obtained by the rapid increase of reduced specific viscosity and the increase of the radius of gyration (determined by light scattering) with increasing degree of neutralization.

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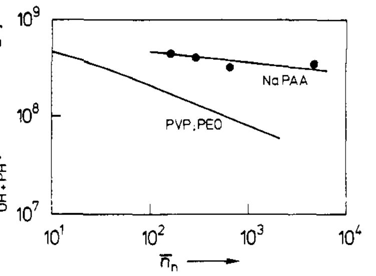

Figure 3. $k_{OH+PH}{}^m$ as a function of chain length.

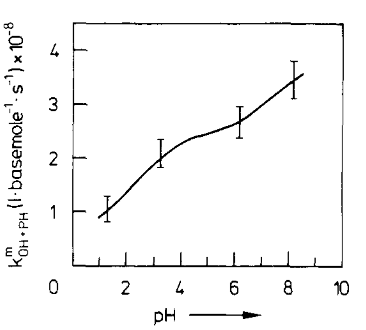

Figure 4. $k_{OH+PH}{}^m$ as a function of pH. Poly(acrylic acid) at 10^{-3} base mol l.$^{-1}$, $\bar{n}_w = 9 \times 10^3$.

If the pH value is further increased, however, the reduced specific viscosity decreases again,[11,15] which suggests a contraction of the coils. The kinetic behavior should reflect the conversion from coil to rod conformation. The results are shown in Figure 4 and corroborate this. Up to about pH 4 the rate constant increases with pH. By inspecting the curve of Figure 4, however, two questions arise which have not yet found satisfying answers. The first one concerns the fact that the smallest value of $k_{OH+PH}{}^m$ found at low pH is still somewhat higher than the value one would expect according to an extrapolation of the curve for PVP and PEO in Figure 3 to $n = 9000$.

The second question results from the finding, that $k_{OH+PH}{}^m$, in contrast to the reduced specific viscosity, does not level off and does not decrease if pH increases to values at which the degree of neutralization approaches 1.0 (pH 8.2), but still increases. It is therefore obvious that the kinetics of the OH attack above pH 5 are strongly influenced by means other than coil expansion. In this connection it should be mentioned that the reactivity of low molecular weight aliphatic carboxylic acids toward OH radicals is known to depend on the state of dissociation. The undissociated forms of the acids react with rate constants two to three times smaller than the dissociated forms.[17] Since a similar trend should hold for polyacids, the additional increase of k_{OH+PH} with pH would become intelligible.

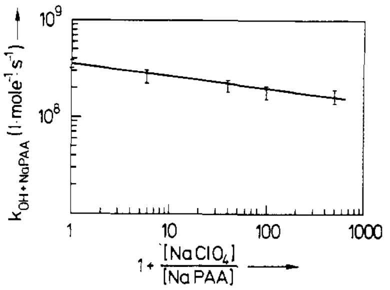

Figure 5. The influence of $NaClO_4$ on the rate constant $k_{OH+PH}{}^m$. Poly(sodium acrylate) at a concentration of 10^{-3} base mol l.$^{-1}$. Plot according to eq 6.

OH + NaPAA, Influence of Added Salt on the Rate Constant. By the addition of low molecular weight salt to a polyelectrolyte solution the intramolecular Coulombic repulsion which causes chain extension is diminished; therefore, a salt effect on k_{OH+PH} should exist if the rate constant depends on conformation. Actually, the influence of added salt should be rather weak since according to Rice and Nagasawa[18] the radius of gyration of sodium poly(vinyl sulfonate) decreases by a factor of about 2 when the concentration of NaCl is varied from 10^{-3} to 1.0 mol l.$^{-1}$. The effect has been treated theoretically by Oosawa.[7] His theory yields the following relationship between the parameter l characterizing the size of the polyion and the concentration of added salt c_s

$$\ln (l_s/l_0) = -A \ln [1 + (\gamma_s c_s/\gamma_P c_P)] \qquad (5)$$

A is a constant. The subscripts s and 0 denote the presence and the absence of salt. γ_s and γ_P are activity coefficients and c_P is the concentration of counterions originating from the polymer. By assuming proportionality between the rate constant $k_{OH+PH}{}^M$ and the parameter l, one obtains

$$\log k_{OH+PH}{}^M \propto -A \log [1 + (c_s/c_P)] \qquad (6)$$

Figure 5 shows the experimental results at constant polymer concentration (10^{-3} base mol l.$^{-1}$) in the presence of sodium perchlorate. This salt does not react with the otherwise highly reactive species produced by the radiolysis of water. Figure 5 demonstrates that $k_{OH+PH}{}^m$ decreases with increasing salt concentration as expected. The decrease appears to follow the trend given by eq 6.

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