Alkaline Degradation of Resorcinol-Formaldehyde Resins: Solid-State NMR, Thermal Adsorption and Desorption Analysis, and Molecular Modeling

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ALKALINE DEGRADATION OF RESORCINOL-FORMALDEHYDE RESINS: SOLID-STATE NMR, THERMAL ADSORPTION AND DESORPTION ANALYSIS, AND MOLECULAR MODELING

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ABSTRACT

Resorcinol–formaldehyde resins, used for alkali metal-cation exchange, were shown to degrade more rapidly in the metallated form compared to the protonated form. Solid-state ^{13}C NMR showed additional peaks in the partially degraded resin corresponding to quinone and other carbonyl functionalities, which are absent in the undegraded resin. Semiempirical molecular orbital calculations were used in conjunction with the experimental data to elucidate the degradation mechanism.

INTRODUCTION

Resorcinol–formaldehyde resin is commonly used as an ion-exchange medium for alkali metal cations. This resin is being evaluated for the removal of radioactive cesium from wastewater as part of cleanup processes at nuclear weapon facilities. It has been observed that over time, the resin loses the ability to absorb cesium. Washing the resin with aqueous alkali results in a dark brown solution, apparently as a result of resin degradation. Previous work at Pacific Northwest Laboratories showed an increase in the free radical content of the resins after exchange with sodium, potassium, and cesium hydroxides, which suggests a free-radical degradation mechanism [1]. In this paper we report on the experimental and computational studies carried out to elucidate the mechanism of degradation of the resorcinol-formaldehyde resins.

EXPERIMENTAL METHODS

Synthesis of Resorcinol–Formaldehyde Resin

The synthesis of the resin is a modification of the general synthetic method for the preparation of phenolic resins [1, 2]. Sixty-six grams (0.6 mol) of resorcinol were mixed in a fume hood with 100 mL of 6 M KOH (0.6 mol) and 500 mL of deionized water in a large, covered Petri dish. The stirred mixture was maintained at 90°C for 1 hour. The resulting solution was cooled to room temperature before 175 mL of 37% formaldehyde solution (2.2 mol) was added with stirring. Some heat was evolved during this step. The uncovered solution in the Petri dish was transferred to a vented oven located in a hood. The oven and solution were maintained at 100°C overnight to effect curing of the resin. A minimum time of 1 hour at 100°C appeared to be necessary for adequate crosslinking of the resulting resin. After that, removal of the water and excess formaldehyde took place. When dry, the resin was mechanically ground and sized using a series of sieves. The resin was washed with deionized water and treated to generate the desired sodium or hydrogen form. Excess sodium hydroxide (2 or 6 M) was passed through a column of the resin to prepare the sodium form; 2 M HNO_3 was passed through a column of the resin to prepare the hydrogen form.

Measurements

Solid-state ^{13}C-NMR spectra were acquired on a Bruker MSL 200 spectrometer operating at 50.3 MHz with cross polarization and magic angle spinning at 4.2 kHz in a 7-mm rotor. A 90° pulse was used with a 3-second delay between pulses to obtain the ^{13}C CP-MAS spectra. ^{133}Cs spectra were obtained at 26.2 MHz with magic angle spinning using a 90° pulse and a 3-second delay. Samples had to be carefully packed and sometimes repacked several times in the rotor to get to the desired spinning rate of 4.2 kHz.

Thermal adsorption and desorption studies were performed on a Stanton simultaneous TGA/DTA unit interfaced to a mass spectrometer. Samples of 10–15 mg were used. The adsorption studies were undertaken at 35°C. A bubbler containing the liquid (water, hexane, benzene) was used as a way of mixing the adsorbate

with the nitrogen gas. Isopropylamine and ammonia adsorption utilized a 20-mL gas syringe with slow injection of the amine directly into the sample chamber. Once the uptake was complete, a second injection to insure saturation followed. Thermal desorption studies followed the same procedure, with a temperature ramping rate of 10°C/min to 500°C under flowing nitrogen.

Computational Methods

Semiempirical PM3 [3] calculations were performed with either the MOPAC 6.0 [4] program and the Insight II graphical interface, produced by Biosym [5] on a Silicon Graphics Indigo 2 workstation, or with the MOPAC 7.0 program on an IBM 590 workstation. All PM3 geometry optimizations were performed in Cartesian coordinates without symmetry constraints, using the PRECISE keyword, which improves the convergence criteria by a factor of 100. In order to accurately compare the energies of open and closed shell species, all calculations were performed with the unrestricted Hartree–Fock (UHF) method. The PM3 lithium parameters of Anders [6] were used as an external parameter set.

RESULTS AND DISCUSSION

Samples of the resin were obtained which had been stored for 18 months at ambient temperature in regular atmospheric conditions, and no steps were taken to exclude moisture or oxygen in order to compare the degradation behavior of the protonated and metallated forms. The ^{13}C spectra are shown in Fig. 1. The protonated resin for the ^{13}C CP-MAS spectrum was stirred in deionized water for 3 days and dried in order to remove any residual monomer and/or degradation products. The spectrum (1a) of this sample shows overlapping peaks in the 15–35 ppm region, corresponding to the methylene bridging carbons, and several overlapping peaks in the 105–160 ppm region, corresponding to the aromatic carbons. A sample of the protonated resin was stirred for 3 days in 2.0 M lithium hydroxide, then washed with deionized water and dried. The NMR spectrum (1b) of this sample shows the appearance of new resonances above 160 ppm, which are consistent with the formation of quinone, carboxylic acid, and other carbonyl functionalities. New resonances also appeared in the 40–100 ppm region as a broad band and indicated the formation of aliphatic carbons adjacent to oxygen and is consistent with the oxidation of the resins [7]. Thus, it appears that the resorcinol–formaldehyde resin degrades more rapidly as the alkali metal salt.

The ^{133}Cs solid-state spectra of the resins are shown in Fig. 2. Freshly prepared resin (less than 30 days old) in the cesium form, prepared by using CsOH instead of KOH as described in the Experimental Section, shows a single peak with 2 shoulders, centered at −16.7 ppm relative to cesium perchlorate (2a). This peak would correspond to the cesium atom bound to the phenolic oxygen atoms, with the different ring positions and orientations giving rise to slightly different chemical shifts, as indicated by the shoulders. A substantially different picture emerged when the protonated resin was exchanged with cesium hydroxide over a period of 2 weeks. Figure 2(b) shows the cesium spectrum of the resin which was exchanged in a 2 M Cs^+ solution buffered to a pH of 8.0 using an acetic acid–sodium acetate system.
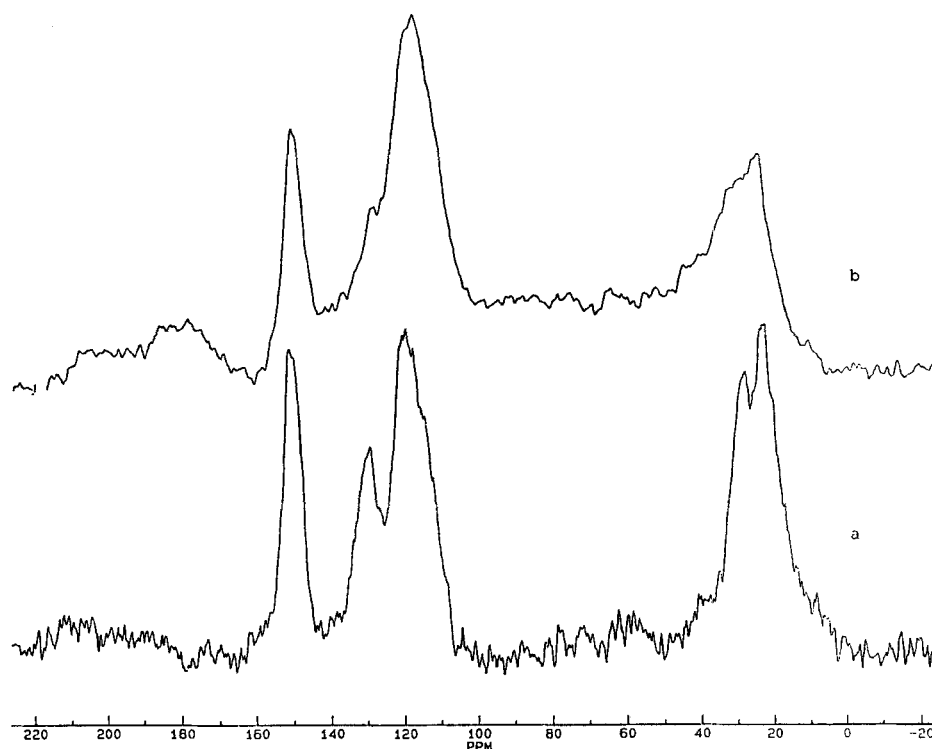
FIG. 1.   CP-MAS ^{13}C-NMR spectra of resorcinol–formaldehyde resin. (a) 3 days in deionized water. (b) 3 days in 2.0 M LiOH.

The spectrum consists of two overlapping peaks centered at 4.7 and −36.2 ppm. The protonated resin was also exchanged in an unbuffered 2.0 M CsOH solution, and the spectrum is shown in Fig. 2(c). In the unbuffered case, two additional peaks appear, which presumably correspond to additional cesium binding sites. The large change in chemical shifts is indicative of the formation of new binding sites, most likely the formation of quinone groups and other carbonyl functionalities, because of the degradation of the resin. The nature of the binding sites is not yet fully understood.

The degradation of the metallated resin was confirmed by an aging study over a period of about 6 months. Figure 3(a) shows the ^{133}Cs solid-state spectrum of newly prepared (less than 30 days old) cesium resin, which consists of a broad, unsymmetrical peak spanning about 100 ppm. After storage for 6 months at room temperature, the peak became narrower and was shifted downfield, indicating a change in binding sites consistent with oxidative degradation of the resin, as shown in Fig. 3(b). Thus, the study of the cesium binding sites at high cesium loading is complicated by the metal-catalyzed degradation of the resin.

The thermal decomposition of the resins was monitored by mass spectra of the desorption products. The samples studied included freshly prepared resin prepared in the sodium form, an aged sample of the same type resin, and resin which had been exchanged with cesium hydroxide as described above. Between 50 and 150°C,
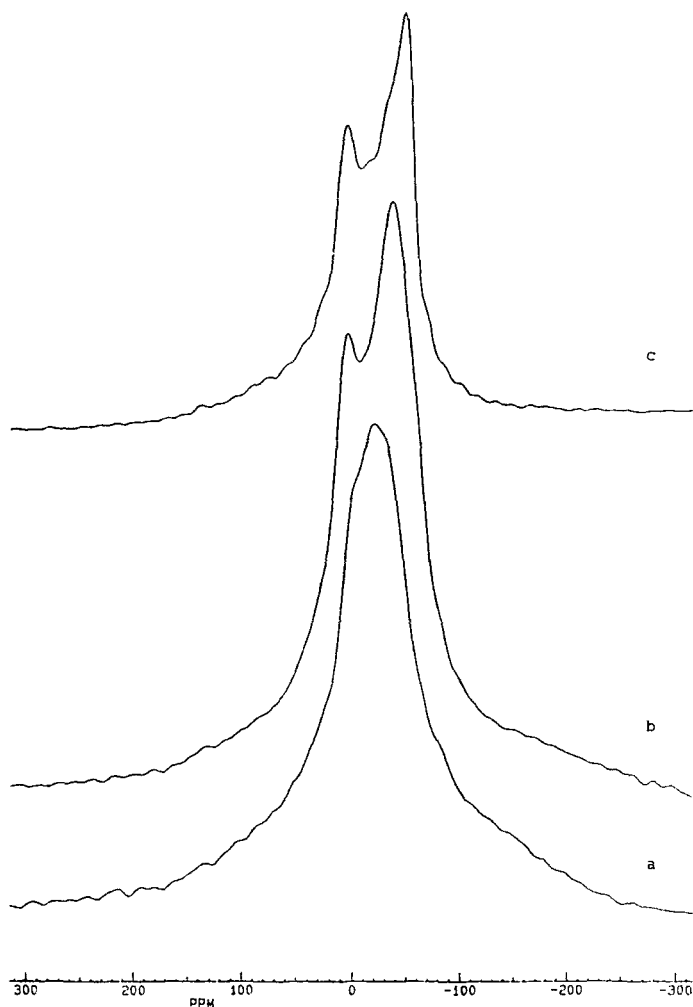
FIG. 2. ^{133}Cs-NMR solid-state spectra of resorcinol–formaldehyde resin. (a) New resin prepared in cesium form. (b) Exchanged with 2.0 M Cs$^+$ at pH 8.0 for 2 weeks. (c) Exchanged with 2.0 M unbuffered CsOH for 2 weeks.

only water desorption was observed in each of the samples. Between 200 and 500°C the water desorption leveled off and carbon dioxide desorption began. No phenol, formaldehyde, benzene, or other detectable organic species were released from the sample. The molecular structure and composition of this material must be such that under nonoxidative conditions, carbon dioxide is easily released. The results are summarized in Table 1. It appears, based on these results, that the aged resin exhibits some early structural or compositional changes relative to the new resin. All samples exhibit similar water contents, but the new resin, and those exchanged at pH 8, appear to have retained more of the carbon/oxygen functional groups than the aged resin or those resins exchanged at a high pH.
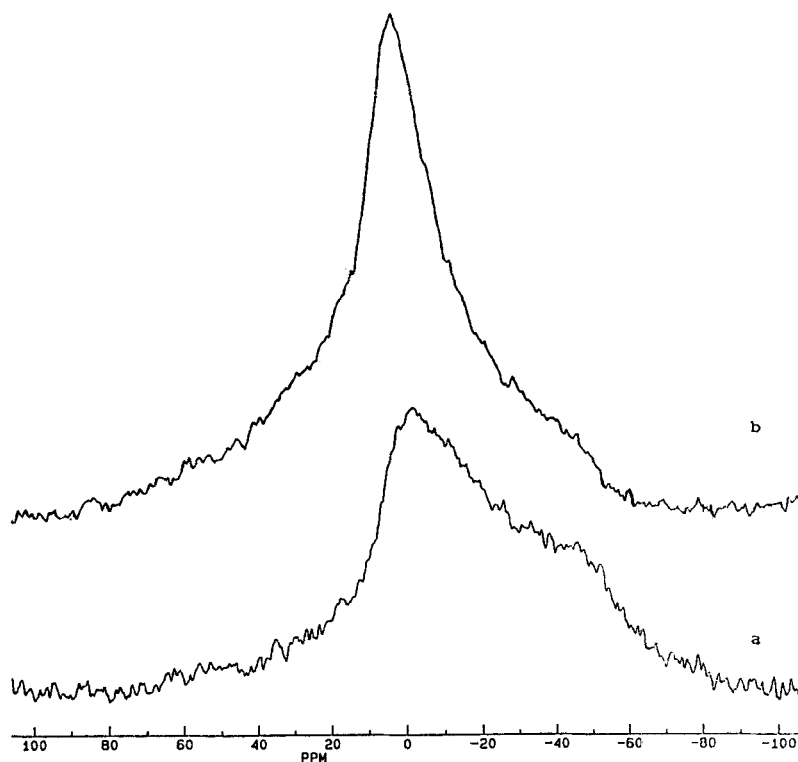
FIG. 3. ^{133}Cs solid-state spectra of cesium-exchanged resorcinol–formaldehyde resin.
(a) Newly prepared resin. (b) Aged for 6 months at room temperature.

TABLE 1.   Thermal Desorption Data for Resorcinol–
Formaldehyde Resins as Determined on a Stanton Simultaneous
TGA/DTA Unit Interfaced with a Mass Spectrometer

Resin	% Water desorbed	% CO_2 desorbed
New, unexchanged	10	22
Aged	10	16
2 M CsOH pH 8 (7 days)	10	20
2 M CsOH pH 8 (14 days)	10	20
2 M CsOH unbuffered (7 days)	10	15
2 M CsOH unbuffered (14 days)	12	17

The adsorption analysis on the new resins on a Stanton TGA/DTA unit interfaced with a mass spectra showed that the water and hexane uptakes were 10 and 6% by weight, respectively, indicating the presence of micropores in the resin accessible to molecules less than 4 Å in diameter. The pore size of less than 4 Å also explains its selectivity for the Cs $^+$ cation. No benzene, isopropylamine, or ammonia adsorption was detected both for the new and the aged resins. The absence of ammonia adsorption is significant, as this indicates the lack of residual acidic sites in the resins and that formation of a significant concentration of the acid functionality in the aged resins may be ruled out. Thus, the new cesium adsorption sites observed in the resin exchanged in the highly alkaline medium appear to result from the formation of quinoid functional groups, rather than from deprotonation of additional phenolic groups.

Two resorcinol rings connected by a methylene bridge were used as a model system for the computational study of the degradation mechanism, as shown in Scheme 1. In the proposed mechanism, in the first step the benzylic methylene
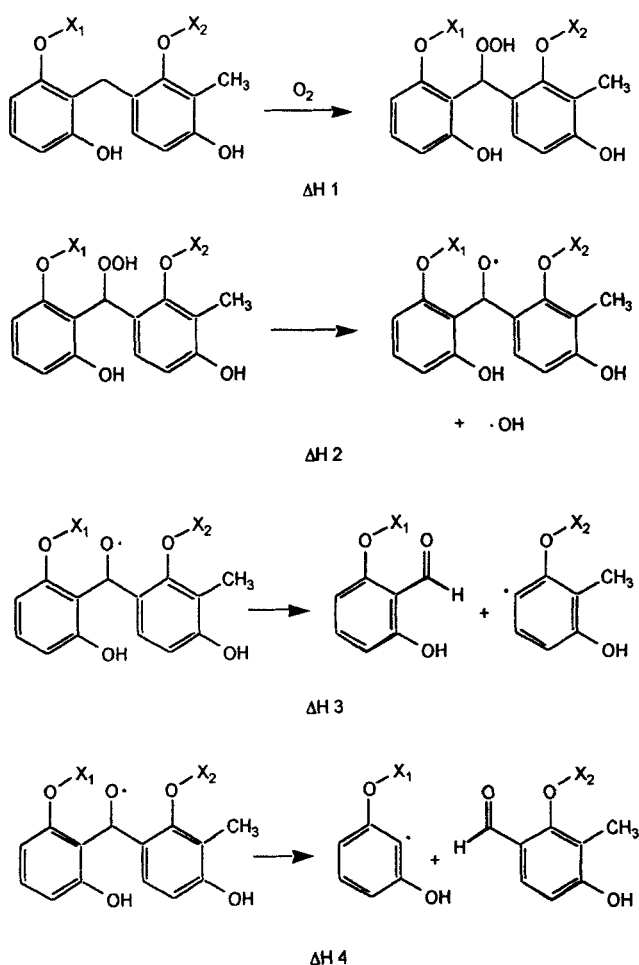
SCHEME 1. Proposed degradation mechanism of resorcinol–formaldehyde resin.

bridge is attacked by the molecular oxygen, forming the hydroperoxide, which decomposes into radicals in the second step. This radical can further decompose in either of two ways, both leading to the formation of an aldehyde and a phenyl radical. These phenyl radicals will react further, leading to the mixture of carbonyl-containing functionalities. Lithium was used as the alkali metal counterion, since no semiempirical parameters have been developed for the other alkali metals. This proposed mechanism is analogous to the known mechanism of oxidative degradation of polystyrene [8]. The reaction enthalpies were determined by the difference between the calculated heats of formation of the reactants and products, except that the heat of formation of oxygen was taken as zero by convention. It should be noted that Hartree–Fock calculations generally do not give very accurate energies for diatomic molecules, therefore the absolute ΔH values in the first two steps should not be taken too literally. The relative reaction energies are much more accurate, as the error in the diatomic heat of formation cancels in a comparison of similar reactions. The results are summarized in Table 2.

The model calculation data, corresponding to Scheme 1, in Table 2 indicate that the lithiation of the resin substantially lowers the energy of the degradation steps. The hydroperoxide, formed by oxidation of the resin, is stabilized by over 6 kcal/mol by the first lithiation, and even more by subsequent lithiation. Decomposition of the hydroperoxide to the free radicals is slightly favored by the first lithiation, and highly favored by the second displacement. The subsequent degradation steps are also favored in the lithiated resin, apparently as a result of the strong coordination of the carbonyl oxygen to the lithium ion, which has been previously reported [9, 10]. Although the metal effect will likely be stronger for lithium than for the other alkali metals, a similar lowering of the reaction energies would be expected with the other metals as well. The formation of aldehyde functionalities (steps 3 and 4) is consistent with the formation of the carbonyl carbons observed in the NMR spectra, as is the formation of quinone groups from further reaction of the hydroquinone radicals. The increased formation of free radicals in the metallated resins has been previously observed [1]. Based on our experimental results and taking into account the calculations on the model systems, we conclude that the most likely degradation mechanism involves the formation of hydroperoxides, which subsequently form free radicals leading to chain cleavage, and that the hydroperoxides and radicals are more easily formed in the metallated resins.

TABLE 2. Calculated Reaction Enthalpies (kcal/mol) for the Degradation Steps of Resorcinol–Formaldehyde Resins Corresponding to Scheme 1

X_1	X_2	$\Delta H\,1$	$\Delta H\,2$	$\Delta H\,3$	$\Delta H\,4$
H	H	−18.6	+31.9	−3.4	−1.4
Li	H	−24.8	+30.0	−15.4	+1.7
Li	Li	−26.5	+17.6	−4.5	−3.7

CONCLUSIONS

The degradation mechanism of resorcinol–formaldehyde resins has been investigated. The carbon-13 NMR spectra indicate the formation of quinoid and other carbonyl functionalities in the partially degraded resin, which appear more rapidly in the presence of alkali metal hydroxides. Cesium-133 spectra clearly show the formation of additional cesium binding sites with long-term exposure to highly alkaline solutions of cesium hydroxide. The lack of ammonia adsorption indicates that these sites are not a result of further deprotonation of acidic phenolic groups. The spectra are consistent with the coordination of cesium ions to the carbonyl groups formed by resin degradation. The carbonyl groups are formed as the phenolic groups are oxidized to quinoid groups, and the methylene crosslinks are oxidized to the aldehyde and/or carboxylate groups. Degradation of the resin appears to take place concurrently with metal ion absorption in alkaline solution. This degradation changes the metal binding sites, and thus the chemical shifts of cesium in the NMR spectra. Overall, the proposed degradation mechanism, supported by semiempirical molecular orbital calculations, is consistent with the experimental data.

ACKNOWLEDGMENTS

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