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Complex Ion Kinetics. Reaction Rates on Ion-Exchange Resins Compared to Those in Water

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A comparison has been made between the rates in water and on an ion-exchange resin for the aquation of $[(NH_3)_5CoOReO_3]^{2+}$ and $[(H_2O)_5CrCl]^{2+}$ and for the ^{18}O isotopic exchange of water with $[(NH_3)_5Co(OH_2)]^{3+}$ and ReO_4^-. The rate of water exchange on $[(NH_3)_5Co(OH_2)]^{3+}$ was not changed by association with Dowex 50W resins. Aquation of $[(NH_3)_5CoOReO_3]^{2+}$ and water exchange on ReO_4^- had modified pH dependencies when associated with a resin. With the cobalt complex the rates were faster on the resin in the acidic region and slower on the resin in the basic region. A new term in the rate equation was observed when ReO_4^- was on the resin, first order in H^+, while the other terms appear to be unchanged. Aquation of $[(H_2O)_5CrCl]^{2+}$ was much slower when it was absorbed on the resin. This was related to the known ionic strength effect of the reaction.

Introduction

Ion-exchange processes have played a highly significant role in studies involving reactions of inorganic and complex ions. Use of ion-exchange resins has been made in determining the charge of ions,[2] the degree of polymerization,[3] the number and type of products of a reaction,[4] and the rate of reaction[5] and in preparative experiments.[6] It has been especially valuable in the reaction product separation of complex ions for analytical[7] and preparative [8] purposes. Considerable time is required for many of these separations during which reactions may occur on the complex ions being separated. These reactions may or may not differ from those occurring in the aqueous phase and can occur during the process of absorption and/or desorption from the resin or during association with the resin. Considerable effort has been made in the study of ion-exchange resins as catalysts for many reactions[9] and the case of an absorbed ion reacting to form a new ion during chromatographic separation has been mathematically developed.[10] Hydrolysis of polypeptides by reaction with complexes immobilized on ion-exchange resins has been of extreme value in recent years.[11] The question of changes in rates of reaction due to interaction with the resin does not appear to have been directly measured. In a qualitative sense it is generally accepted that for the usual inert Werner type complexes neither the products nor the reaction rates change drastically when absorbed on a resin.

This study compares reaction rates on a resin with those in water for four fairly representative systems: aquation of $[Co(NH_3)_5OReO_3]^{2+}$ and $[Cr(OH_2)_5Cl]^{2+}$ and the ^{18}O water exchange with $[Co(NH_3)_5OH_2]^{3+}$ and with ReO_4^-. The products of these reactions were found to be identical on the resin and in water and the kinetics in aqueous media is well known. It was hoped that the results of this study would allow a prediction of the magnitude and direction of changes in reaction rate of complex ions when associated with ion-exchange resins.

Experimental Section

A. Aquation of Resin–$[Co(NH_3)_5OReO_3]$ in Water. $[Co(NH_3)_5OReO_3](ReO_4)_2$ was prepared as previously described.[6] Dowex 50W-X4 or 50W-X2 (50–100 mesh) was freshly purified each day by exhaustive washing with 6 *M* HCl, 2 *M* NaOH, 1 *M* NaCl, and water leaving it neutral in the sodium ion form.

About 2 ml of resin was suspended in 25 ml of pure water at 0° and about 50 mg of complex was added. With stirring it took about 5 min for the complex ion to dissolve and be absorbed by the resin. The resin complex was collected on a filter and washed exhaustively with water (0°). At this point it was about 50% in the complex form. It was then added to 100 ml of buffer solution or water at the appropriate reaction temperature and approximately 0.3-ml aqueous samples were collected at timed intervals. Stirring was intermittent. The $[ReO_4^-]$ in each of these samples was determined by exact dilution of 100 μl to 50.00 ml with a color-developing solution consisting of HCl, acetone, $SnCl_2$, and either DMG[12] or furil dioxime (FDO).[13] After 3 hr of color development the light absorption was measured at 445 nm (DMG) and 532 nm (FDO), and $[ReO_4^-]$ was determined from standard curves. Graphs of $-\ln(1 - F)$ vs. time were linear over at least 3–4 half-times giving values for k_{obsd} (Table I, Figure 1).

Buffer solutions utilized 2,6-lutidine–HCl mixtures, a poorly coordinating amine, since the reaction is general acid–base catalyzed. However, they were not entirely satisfactory and the solution pH changed upon addition of the resin. This was due apparently to replacement of Na^+ from the resin by 2,6-lutH^+ with a consequent increase in solution basicity. This occurred instantaneously however, and the final pH represents the reaction conditions. The concentration of either cobalt complex in solution at any time in the reaction was extremely small being estimated at less than 0.001 of the total cobalt. This was maintained by having the resin less than two-thirds saturated with the cobalt complex.

B. Oxygen Exchange between Resin–ReO_4 and Water. $NaReO_4$ (^{18}O enriched) was prepared from $HReO_4$ by equilibration with $H_2{}^{18}O$ (1 hr at 25°) followed by neutralization with solid NaOH. Recrystallization was from MeOH–acetone solution. Dowex 1-X4 (50–100 mesh) was washed with 8 *M* HCl, 4 *M* NaOH, and saturated NaCl solutions in that order and then exhaustively with twice distilled water. CsCl and NaCl were recrystallized from water until their solutions were neutral. 2,6-Lutidine was distilled and the middle third used with HCl to formulate buffer media.

To a 5.0-cm column containing approximately 20 ml of freshly cleaned and washed resin–Cl[14] at 0° 150 ml of a cooled solution containing 5.0 g of $NaReO_4$ (^{18}O enriched) was added. This constituted about two-thirds of the capacity of the resin. The resin–ReO_4 was washed with cold water, dried by aspiration, and added to 100 ml of water or appropriate buffer solution at the proper temperature in a water bath. (On occasion, the resin–Cl was prewashed with the buffer solution or converted to the OH^- form before $NaReO_4$ addition.)

Table I. Rate Constants of ^{18}O Exchange between Resin$^+$–ReO_4^- and Water (25°, Dowex 1-X4 (50–100 Mesh))

Run	Acidity (makeup)	$[H^+]_{measd}$, *M*	% Re in soln	p*k**	p*k**$_{calcd}$^{e}	$10^4 k_H$^{e}
1	7.3[a,b]	7.1×10^{-7}	0.02	7.88	7.85	
2	5.0[a]	1.3×10^{-7}	0.02	7.82	7.85	
3	3.0[a]	1.4×10^{-4}	0.05	7.44	6.17	1.50
4	3.0[a]	2.0×10^{-4}	0.08	7.39	5.18	1.28
5	0.005	2.2×10^{-3}	0.16	6.22	3.78	1.49
6	0.01	4.1×10^{-3}	0.34	5.58	2.90	1.68
7	0.005[c]	2.2×10^{-3}	0.17	6.24	3.78	1.30
8	0.005[d]	2.0×10^{-3}	0.14	6.28	3.87	1.61
9	0.005 (OH^-)	5.0×10^{-11}	0.07	6.31	6.11	
10	0.01 (OH^-)	3.2×10^{-12}	1.04	6.06	5.81	

[a] pH. [b] 2,6-Lutidine buffer, 0.02 *M*. [c] Dowex 1-X2 (100–200 mesh). [d] Reused resin. [e] Calculated on the basis of the established rate equation in water. See text.

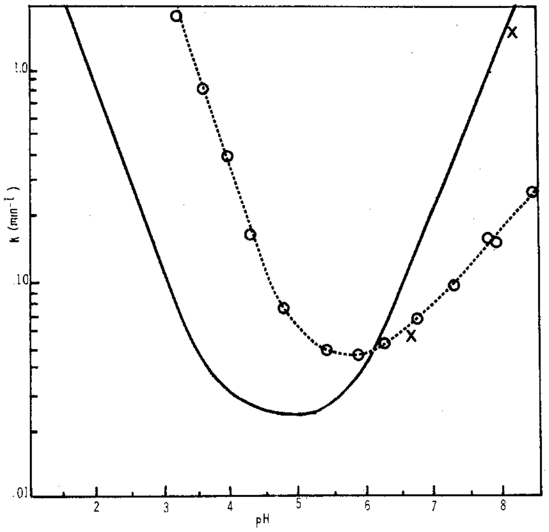

Figure 1. Rate constants of $[(NH_3)_5CoOReO_3]^{2+} \rightarrow [(NH_3)_5Co(OH_2)]^{3+} + ReO_4^-$ (25°): ——, water; - - - - -, resin, 0.01 *M* 2,6-lutidine + HCl buffer.

At timed intervals, approximately 1.0-ml samples of the resin–ReO_4 were collected by filtration and washed with 50% saturated NaCl solution, and the NaCl solutions (containing 90% of the $NaReO_4$) were cooled in an ice bath and treated with 0.5 ml of a saturated CsCl solution to precipitate $CsReO_4$(s). The $CsReO_4$(s) was collected on a microfilter, washed with alcohol and anhydrous ether, and quickly dried over $Mg(ClO_4)_2$. The oxygen in $CsReO_4$ was converted to CO_2 as previously described[15] and the mass 46/(44 + 45) ratio was determined on a Nuclide dual-collector mass spectrometer. The isotope ratios were normalized to 0.00400 for a standard CO_2 sample. Graphs of $-\log (N - N_\infty)$ vs. time (typically 6–10 points) were linear (Figure 2) and gave reaction half-times ($t_{1/2}$) from which k^*, the rate constant of exchange, was evaluated utilizing the equations

$$R = (4[ReO_4^-][H_2O]/4[ReO_4^-] + [H_2O])(0.693/t_{1/2})$$

$$k^* = \frac{R}{[ReO_4^-]} = 4\left(\frac{0.693}{t_{1/2}}\right) \text{sec}^{-1}$$

The latter equation is a modification of that previously used[15] changing the standard states of H_2O and resin–ReO_4 to unity.

The supporting electrolyte caused a partial replacement of ReO_4^- from the resin. An estimate of the concentration of ReO_4^- in solution was obtained by analyzing the final solution after each rate run for ReO_4^- by a colorimetric method.[13] The maximum found in solution was about 1% of the total with most samples showing a considerably smaller value.

C. Water Exchange with $[Co(NH_3)_5OH_2]^{3+}$. $[Co(NH_3)_5OH_2](ClO_4)_3$ was prepared by a standard method[16] and enriched by dissolving 5 g in 25 ml of oxygen-18-enriched water (^{18}O content 1.6 atom %) to which several drops of perchloric acid had been added. The solution was heated at 60° for 4 hr and the compound was allowed to crystallize by cooling it in an ice bath and adding perchloric acid. $[Co(NH_3)_5OH_2](ClO_4)_3$ was collected by filtration and dried in a desiccator over $Mg(ClO_4)_2$ at room temperature and atmospheric pressure.

Samples (0.4–0.8 g) of the enriched $[Co(NH_3)_5{}^{18}OH_2](ClO_4)_3$ were dissolved at 0° in about 10 ml of water to which a few drops of $HClO_4$ had been added. This solution was passed through a 2–3-in. column of Dowex 50W-X2 ion-exchange resin which absorbed the aquopentaamminecobalt(III) ion. The resin was immediately transferred to a flask containing about 50 ml of dilute $HClO_4$ of known concentration in a thermostated bath (±0.05°).

The rate of H_2O exchange was followed by periodically removing aliquots of the resin to a column and quickly eluting the aquopentaamminecobalt(III) ion with 3–6 *M* HCl. The eluent was collected at 0° in a flask containing several milliliters of a saturated solution of NaBr in hydrobromic acid. The precipitate of $[Co(NH_3)_5OH_2]Br_3$ was washed several times with water and then with methanol and dried under vacuum at room temperature.

Analysis for ^{18}O was conducted by a previously described[17] modification of the method of Anbar and Guttman.[18] Samples were converted to CO_2 by heating with a 1:1 mixture of mercury(II) cyanide and mercury(II) chloride in break-seal tubes. The carbon dioxide was separated from the other gases formed by vapor-phase chromatography, using silicone oil on Chromosorb P, and analyzed on the mass spectrometer, the 46/(44 + 45) ratio being measured. The values obtained were compared to a standard sample of normal CO_2, for which the ratio was arbitrarily assigned a value of 0.00400.

D. Aquation of $[Cr(H_2O)_5Cl]^{2+}$. Chloropentaaquochromium(III) sulfate was prepared by the method of Moore and Basolo.[19] Its purity was checked by ion-exchange separation. No polymers, $Cr(H_2O)_6^{3+}$, or $[Cr(Cl)_2(H_2O)_4]^+$ could be found. The rate of aquation was measured for the $[Cr(H_2O)_5Cl]^{2+}$ ion both when it was absorbed on an ion-exchange resin and when solutions of the ion were in the absence of the resin.

Dowex 50W-X8 exchange resin, hydrogen form, was used (4–5 g per sample). The resin was cleaned by successive washings with 6 *M* HCl, 0.1 *M* NaOH, 6 *M* HCl, acetone, saturated NaCl solution, and water. The resin was placed in a beaker with 10–15 ml of dilute $HClO_4$ at 0° and 0.6 g of $[Cr(H_2O)_5Cl]SO_4$ was added with stirring. The solution above the resin was decanted and the resin, containing the absorbed $[Cr(H_2O)_5Cl]^{2+}$ ion, was transferred to the flask containing 50–60 ml of dilute $HClO_4$. The temperature of the flask and its contents was maintained at 50 (±0.01)° by means of a thermostated bath.

The rate of aquation was measured by monitoring the chloride ion concentration in the solution above the resin. Aliquots were periodically removed and the Cl^- content was determined by displacement of SCN^- from $Hg(SCN)_2$ by Cl^- and the subsequent reaction of SCN^- with Fe^{3+} to form the colored $[Fe(SCN)]^{2+}$.[20] One milliliter of the sample, 0.5 ml of 0.2 *M* $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ in 9 *M* HNO_3, and 0.5 ml of a saturated ethanol solution of $Hg(SCN)_2$ were mixed and diluted to 10 ml. Absorbance was measured on a Beckman DU spectrophotometer at 460 nm and compared with standards.

The rate of aquation of $[Cr(H_2O)_5Cl]^{2+}$ in solution with no resin was determined by several methods. Aliquots of the solution were removed and cooled to 0°. Dowex 50W-X8 ion-exchange resin was then added to remove the $[Cr(H_2O)_5Cl]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ ions from solution. The concentration of Cl^- remaining in solution was measured by the $[Fe(SCN)]^{2+}$ method. The reaction was also followed by spectrally measuring the disappearance of the ion at 450 nm. A thermostated cell was used to maintain a constant temperature of 50°. Also the rate of aquation was measured by following the disappearance of $[Cr(H_2O)_5Cl]^{2+}$ at 230 nm, using a Cary Model 14 spectrophotometer. In this case, aliquots of the solution were removed from

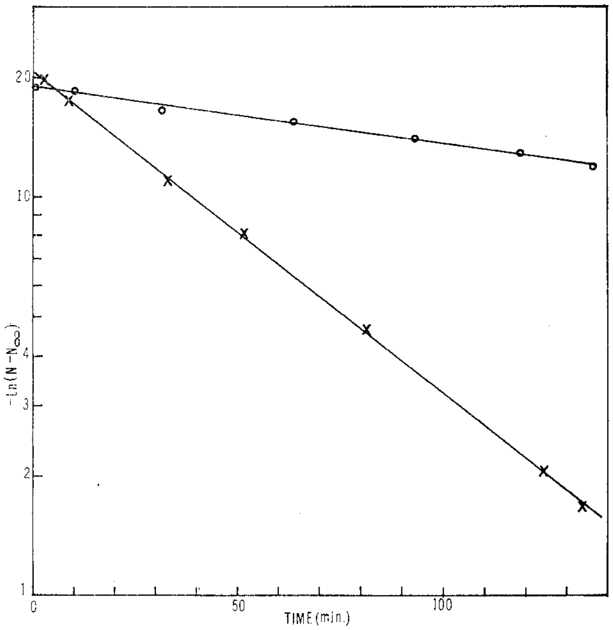

Figure 2. Rate of $H_2{}^{18}O$ exchange with ReO_4^- (25° on Dowex 1-X4): ○, 0.01 *M* NaOH; ×, 0.01 *M* HCl.

a constant-temperature bath and stored ~0° until absorbance measurements were made. Essentially the same results were obtained with the three methods, the highest precision being with the $Fe(SCN)^{2+}$ analysis scheme.

Sulfate ion from the starting complex did not affect the measured rates in solution. Its concentration was small but differed widely with the analysis method. Thus its presence did not significantly modify the acidity or ionic strength of the media.

Results and Discussion

A. Aquation of $[Co(NH_3)_5OReO_3]^{2+}$. These kinetic studies provided linear first-order graphs whose slope was independent of the previous history of the resin and of the resin load. Figure 1 gives the rate constants of aquation as a function of pH in water solution (0.02 *M* buffer), compared with that for the resin-associated ion. In water solution, (0.02–0.17 *M* 2,6-lutidine–HCl buffer), the rate expression is

$$k = k_0 + k_H[H^+] + k_{OH}[OH^-]$$

The basic features of the curves are the same. However the rate constant is enhanced by a factor of about 10 in the acidic region when the ion is associated with the resin while the order with respect to H^+ appears not to change. The activation energy in both the acidic and basic regions remained the same as in solution (±1 kcal), 8.4 and 14 kcal/mol, respectively.[6] In basic media the order with respect to $[OH^-]$ drops. This conclusion is somewhat clouded however by the fact that two runs without buffer, those marked ×, gave different results. Thus in the basic region the amine–acid buffer has an unexpected effect. The k_0 path is not greatly enhanced when the reacting ion is resin associated but due to the overlapping contributions of the three paths either a slightly diminished or enhanced value would not be noted.

B. ReO_4^-–H_2O Isotopic Oxygen Exchange. The individual rate runs at constant pH showed a linear relationship between $-\ln(1-F)$ and time (Figure 2) in both acidic and basic media. Thus all sites of resin–ReO_4^- association are kinetically equivalent on the time scale of the oxygen exchange and the water diffusion between resin and solution is also comparatively rapid. The solution pH changed upon addition of the resin–ReO_4^- due to exchange and replacement of buffer ions with those on the resin. Less than 2% exchange was induced by the separation method as evidenced by the zero-time exchange. A summary of the results is given in Table I. The effect of light and of the 2,6-lutidine buffer was small and degree of cross-linking (×2 or ×4) or new or reused resin caused no appreciable rate effect.

Since the acids, bases, and buffers in solution caused a partial replacement of ReO_4^- from the resin which exchanges in solution with known[15] rate constants, the fraction so displaced was analytically determined for each run and is given in column 4 of Table I.

In general the rate constant of oxygen exchange increased in acid and base with a minimum in the neutral region. This parallels the behavior of ionic ReO_4^-.[15] Column 5 gives the calculated pk^* values for each run. If ReO_4^- exchanged with the same rate expression and constants in solution as on the resin, i.e.

$$k^*_{\text{calcd}} = k_0 + k_H[H^+]^2 + k_{OH}[OH^-]$$

then the values in column 6 would result.[15] Within the experimental precision the neutral and basic regions are sensibly equal for ionic and resin-bound ReO_4^-, but in the acidic region the observed rate constants are much too low for the resin–ReO_4^- experiments. A fit to the data in the acidic region was obtained utilizing a reasonable equation

$$k^* = k_0 + k_{H^2}(F)[H^+]^2 + k_H[H^+]$$

where k^* is the measured rate of exchange of ReO_4^- on the resin, k_0 is the pH-independent term known in solution and assumed to be the same on the resin, k_H is the unknown rate constant of exchange for resin–ReO_4^- with a first-order dependence on H^+, and $k_{H^2}(F)$ is the product of the fraction of ReO_4^- in solution (F) and the known rate constant for the $(H^+)^2$ term in solution. The first and last terms correct for the exchange of free aqueous ReO_4^-. The calculated value of k_H is given in column 7 and is essentially constant. Thus it appears that the last term in the rate equation in solution

$$k^* = k_0 + k_{OH}[OH^-] + k_H[H^+]^2 \quad (ReO_4^- \text{ soln})$$

is modified when ReO_4^- is attached to the resin and becomes first order in H^+

$$k^* = k_0 + k_{OH}[OH^-] + k_H[H^+] \quad (ReO_4^- \text{ on resin})$$

The average value of k_H is $(1.49 \pm 0.13) \times 10^{-4}\ M^{-1}\ sec^{-1}$. The apparent change in $[H^+]$ order can be rationalized by picturing the resin as furnishing the positive charge provided in solution by the second hydrogen ion.

The basic conclusion of these experiments is that the ReO_4^-–H_2O exchanging process is not modified extensively by association with an organic resin. Its pH behavior is changed slightly which may be due to the resin serving as a positive charge and assisting another H^+ in kinetically loosening an oxygen of ReO_4^- allowing exchange.

Table II. First-Order Rate Constants for Aquo Exchange between $[Co(NH_3)_5H_2O]^{3+}$ and Solvent (Dowex 50W-X2)

$[HClO_4]$, *M*	Temp, °C	10^4k, min^{-1}	$t_{1/2}$, min
0.1	25	3.25	2132
0.005	25	3.25	2132
1.0	25	3.01	2300
0.05[a]	25	3.38	2050
0.05	50	112.0	62
0.1	50	116.0	60
Neutral[b]	25	3.36	2060
0.05[b]	25	3.15	2200

[a] Dowex 50W-X8. [b] Aqueous solution—no resin.

C. $[(NH_3)_5CoOH_2]^{3+}$–$H_2{}^{18}O$ Exchange. The first-order rate constants of water exchange when $[(NH_3)_5CoOH_2]^{3+}$ is absorbed on Dowex 50W-X2 or -X8 are given in Table II. The rate is essentially independent of acidity (0.005–1 *M*). The last two entries are a repeat of the solution kinetics[16] and

Table III. Rate Constants for Aquation of $[Cr(H_2O)_5Cl]^{2+}$

$[HClO_4]$, *M*	10^6k, sec^{-1}	$t_{1/2}$, min
A. Associated with an Ion-Exchange Resin[a] (No Supporting Electrolyte)		
0.0176	27.8 ± 1.4 (3)[b]	418 ± 19
0.0560	24.4 ± 1.3 (2)	475 ± 25
B. In Aqueous Solution (50 ± 0.1°)		
0.0173	509 ± 67 (5)	23 ± 4
0.0173[c]	155 ± 3 (2)	75 ± 2
0.0161[d]	94.3	122
0.0470[d]	37.0	312
0.0716[d]	27.0	428

[a] At 50.0 ± 0.1°, using Dowex 50W-X8 cation-exchange resin. [b] Numbers in parentheses indicate number of runs included in average reported. [c] Ionic strength of 1.0 *M* maintained with lithium perchlorate. [d] Reference 8. $I = 1.0$ ($LiClO_4$).

are in complete agreement with those results. At 25 and 50° the rate constants for the complex ion absorbed on the resin are essentially the same as observed for the free ion[16] which suggests no change in the energy of activation.

D. Aquation of $[(H_2O)_5CrCl]^{2+}$. The observed values for the first-order rate of aquation are given in Table III. In aqueous solution the ion is sensitive to both acid concentration and ionic strength, decreasing in rate with both increasing acid and increasing ionic strength. When the complex ion is absorbed on the resin, the rate of aquation diminishes by nearly a factor of 20. In order to be sure this effect was real the rate in solution was reevaluated under two experimental conditions. Although the absolute value did not agree with the previous study as well as desired, the effect of ionic strength was confirmed. High ionic strengths, as used in the earlier solution studies, were not advisable in the resin studies since some of the complex ion would be displaced from the resin.

These results show the rate of aquation of $[Cr(OH_2)_5Cl]^{2+}$ to be lowered significantly when associated with an anion-exchange resin, Dowex 50W-X8. One is tempted to relate the sensitivity of this reaction to ionic strength changes in solution to the lowering of the rate when it is absorbed on a resin. The similarity of the environment of an ion-exchange resin and a concentrated salt solution is evident and they do produce the same effect on the rate of reaction.

Conclusions

The ion-exchange process is thought to include a rapid (relative to the reactions being studied) diffusion of solvent from bulk solvent to internal water both bound and free. Further, the process of ion replacement is primarily a diffusion-controlled process.[21] The observed fact that first-order behavior is found for these resin systems (as it is in solution) confirms the comparatively rapid elimination of products from the resin interstices through equilibration with the bulk solvent.

Some kinetic generalizations may be inferred from these results. A. For reactions which are not highly sensitive to their environment, i.e., specific ion effects, pH, and ionic strength, the rate constants in solution and on the resin will be essentially the same. B. Reactions sensitive to the solution pH will have a modified pH pattern on the resin. This may take the form of the resin serving as a positive charge replacing an H^+ in an acid term or may diminish the effect of either H^+ or OH^- due to their reluctance to be active in the matrix of a like-charged resin. C. For reactions which are sensitive to ionic media the resin environment is similar to a high ionic strength solution and the rate changes will mimic those found at high ionic strength.

It is surprising that the effects seen are not larger for it is well established[22] that strong electrolytes are rather highly excluded by the resins.

These experiments have been confined to reactions which are either isotope substitutions or those which normally show first-order behavior. Substitution reactions on complex ions which are normally kinetically dependent on the substituting ion are also of interest especially in the realm of mechanistic interpretation. Such studies are anticipated.

Registry No. $[Co(NH_3)_5OReO_3]^{2+}$, 21350-30-1; $[Cr(OH_2)_5Cl]^{2+}$, 14404-08-1; $[Co(NH_3)_5OH_2]^{3+}$, 14403-82-8; ReO_4^-, 14333-24-5.

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