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The Transition State for Exchange of Protons and Metal Ions in a Carboxylate Ion-Exchange Resin[1]

Julio F. Mata Segreda, Siegfried Lindenbaum, and Richard L. Schowen*

Contribution from the Departments of Chemistry and Pharmaceutical Chemistry,
University of Kansas, Lawrence, Kansas 66045, and the School of Chemistry,
University of Costa Rica, San José, Costa Rica.

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Abstract: The release of protons from Amberlite CG-50 ion-exchange resin into water at 25.0 ± 0.5 °C, induced by lithium, sodium, or potassium ions, is a first-order process with a rate constant of $7.4 \pm 0.4 \times 10^{-3}\ \mathrm{s}^{-1}$. This constant is independent of metal-ion concentration and identity, quantity of resin, and stirring speed under the conditions employed. The rate constant for proton release into protium oxide exceeded that for deuteron release into deuterium oxide by factors of 3.06 ± 0.17 (Na^+) and 3.36 ± 0.38 (K^+). The rate constant k_n for lyon release into binary mixtures of protium oxide and deuterium oxide (atom fraction n of deuterium) is given by the equation $k_n = (7.4 \pm 0.5 \times 10^{-3}\ \mathrm{s}^{-1})(1 - n + [0.70 \pm 0.02]n)^3$. The transition state for proton release from the resin appears to be that for migration of a preformed hydronium ion through the resin matrix. This migration generates a hole which is rapidly occupied by the metal ion.

The exchange of protons and metal ions at macromolecular binding sites is a process of considerable importance in a variety of fields, not least in biochemistry.[2] A simple system susceptible of kinetic study[3] is offered by ion-exchange resins. We report here solvent isotope effect studies which permit a characterization of some features of the transition state for proton release from a carboxylate resin, induced by alkali-metal cations.

Results

These studies were conducted by monitoring the pH of a stirred aqueous solution in contact with a quantity of Amberlite CG50 ion exchange resin, hereafter called "resin". When alkali-metal chlorides were added to the aqueous phase, protons were slowly released from the resin and the pH decreased. No slow proton release was observed from resin in contact with water not containing alkali-metal salts. The release of protons was a first-order process, as the data of Figure 1 demonstrate, after an initial 1–2 min period of swelling and equilibration. The total number of protons released when the external metal-ion concentration was around 0.1 M constituted about 3% of the protons titratable by sodium hydroxide.

Effect of Stirring Speed and Quantity of Resin. With 0.1 M external sodium chloride concentration, the stirring speed was maintained at 1120, 2310, and 3060 rpm and rate constants for proton release 7.41 ± 0.41, 7.40 ± 0.54, and 7.41 ± 0.17 $\times 10^{-3}\ \mathrm{s}^{-1}$, respectively, were obtained. Thus, in this range, the rate constant for proton release is unaffected by stirring

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*Address correspondence to this author at the University of Kansas.

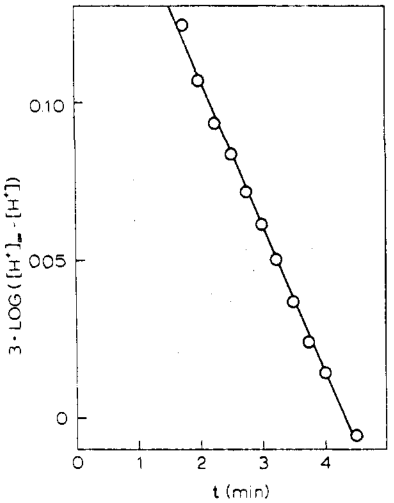


Figure 1. First-order plot of the data for proton release from resin in the presence of aqueous solutions of alkali-metal ion. In this experiment, proton release was induced by 0.1 M sodium chloride from 0.1 g of resin in contact with 10 mL of the aqueous phase. The stirring rate was 2310 rpm.

speed. All further experiments were conducted at 1120 rpm. Experiments in which the amount of resin in contact with 10 mL of solution was varied gave rate constants 10^3k (s^{-1}) for the amount of resin shown in parentheses: 7.41 (0.200 g), 7.70 (0.111 g), 7.60 (0.078 g), 7.50 (0.060 g), and 7.75 (0.055 g). The rate constant for proton release is therefore unaffected by the quantity of resin in the reaction vessel.

Effect of Metal Ion. At 0.1 M external concentration of metal ion, proton release occurred with a rate constant of 7.32 ± 0.19 × 10^{-3} s^{-1} when induced by lithium chloride, 7.41 ± 0.41 × 10^{-3} s^{-1} when induced by sodium chloride, and 7.86 ± 0.22 × 10^{-3} s^{-1} when induced by potassium chloride. The rate of proton release is therefore independent of the identity of the alkali-metal ion. The following rate constants, 10^3k (s^{-1}), were obtained at the sodium chloride concentrations shown in parentheses: 7.41 ± 0.41 (0.100 M), 7.32 ± 0.19 (0.220 M), 7.77 ± 0.08 (0.282 M), 6.93 ± 0.07 and 7.66 ± 0.07 (0.400 M). The resin thus releases protons at a rate independent of the concentration of the ion inducing their release, for metal-ion concentrations 0.1–0.4 M.

Solvent Isotope Effects. The rate of deuteron release from resin, after a period of about 2 min in contact with deuterium oxide, was again first order with a rate constant of 2.42 ± 0.04 × 10^{-3} s^{-1} (when induced by sodium chloride) or 2.34 ± 0.10 × 10^{-3} s^{-1} (when induced by potassium chloride). The overall solvent isotope effect is thus 3.06 ± 0.17 (Na^+) or 3.36 ± 0.38 (K^+).

In binary mixtures of protium and deuterium oxides, the rate constants shown in Table I were obtained. A plot of k_n vs. n (atom fraction deuterium in binary mixture of isotopic waters) is shown in Figure 2.

Discussion

Because the rate of proton release from resin is independent of such quantities as stirring speed and amount of resin, it should be possible to treat the process as an ordinary chemical reaction, with no hydrodynamic or surface effects beyond those encountered in homogeneous processes.

Because the first-order rate constant for proton release is independent of both the concentration and the nature of the metal ion, the transition state for proton release may not contain the metal ion. The rate could be independent of metal-ion concentration if the resin surface were initially saturated with metal ions, but the rate would not be independent of the *nature* of the metal ion. Proton release, on the other hand, occurs only when metal ions are present in the solution. The simplest explanation for these facts is that the metal ion rapidly traps proton-binding sites which are vacated of protons in a slow process. In the absence of metal ion, protons reoccupy the sites and there is no net proton release.

Table I. First-Order Rate Constants for Lyon Release from Resin in Contact with Binary Mixtures of Protium Oxide and Deuterium Oxide (Atom Fraction of Deuterium n), Induced by 0.100 M Sodium Chloride at 25.0 ± 0.5 °C

n	10^3k_n, s^{-1}	n	10^3k_n, s^{-1}
0.000	7.41 ± 0.41	0.558	3.81 ± 0.23
0.119	6.55 ± 0.18	0.656	3.40 ± 0.05
0.235	5.63 ± 0.12	0.780	3.34 ± 0.02
0.330	5.07 ± 0.08	0.993	2.42 ± 0.04
0.431	4.76 ± 0.05		

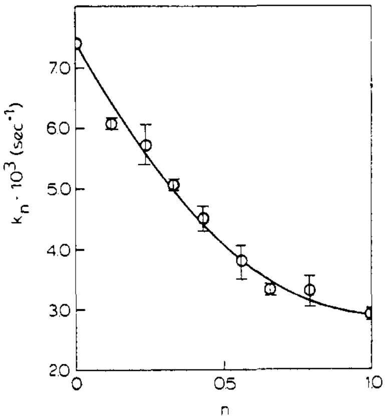
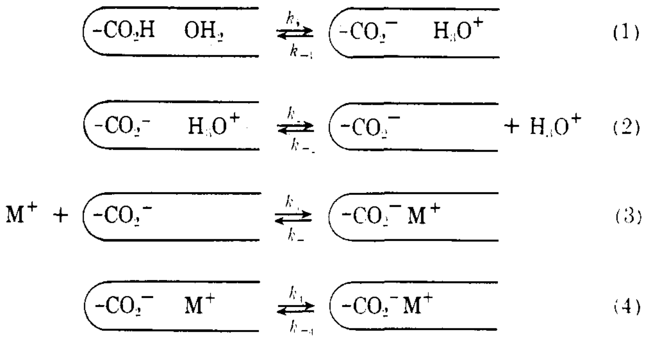


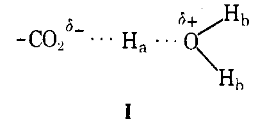
Figure 2. Rate constants for sodium-ion-induced release of lyon from resin in contact with binary mixtures of protium and deuterium oxides, plotted against n, the atom fraction of deuterium in the hydrogenic positions of the aqueous phase. The solid line is the best-fit cubic polynomial.

Scheme I



If we assume that the common binding sites for both protons and metal ions are at the carboxylate centers of the resin and that the proton is bound covalently while the metal ion is bound ionically, then we can write the mechanistic sequence of Scheme I. Here eq 1 represents the ionization of the proton at the binding site, eq 2 migration of the hydronium ion through the resin matrix and its release into the solution (obviously a complex sequence of events), eq 3 the entrance into the resin and migration to the binding site of the metal ion, and eq 4 the securing of the metal ion at the binding site (possibly involving solvation changes or structural alterations of the matrix).

The lack of kinetic dependence on metal ion excludes eq 3



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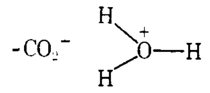

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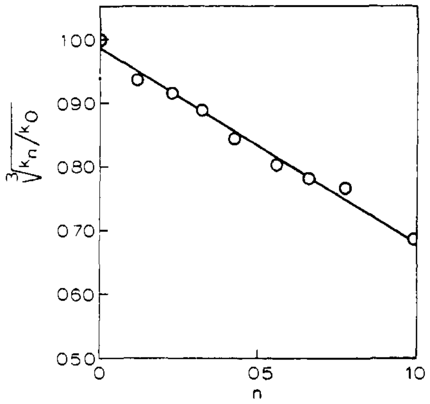

Figure 3. The cube root of the solvent isotope effect, which is linear in n, vs. the atom fraction of deuterium in the aqueous phase.

and 4 as rate limiting. Thus either eq 1 or 2 should determine the rate. The transition state for eq 1 should have structure **1** while that for eq 2 should have structure **2**. In a fortunate case, these two can be distinguished by the magnitude of the rate constant. The character of the solvent isotope effect should provide a further test of any hypothesized structure. We will argue that the results favor structure **2** with migration of the hydronium ion, eq 2, rate determining.

If structure **1** were correct, the observed rate constant for proton release should be that for the proton-switch step in the ionization of an acid of pK_a around 8 (this is the average pK_a of resin carboxyl groups, determined as described in the Experimental Section). The expected proton-switch rate constant can be estimated as follows. If the ionizing species were an acid in homogeneous solution, the analogue of the k_2 process (call it the k_2' process) would be simply diffusion of the hydronium ion away from the anion. This is in fact the rate-determining step for ionization of acids in homogeneous aqueous solution.[4] For an acid of pK_a 8, eq 5 should be true. For k_2' to be rate

$$10^{-8} = k_1 k_2'/k_{-1}k_{-2}' \qquad (5)$$

determining, $k_2' \sim k_{-1}/10$. We know[4] that $k_{-2}' \sim 10^{10}$ M^{-1} s^{-1}. Thus $k_1 = 10^{-8}(k_{-1}k_{-2}'/k_2') \sim 10^{-8}(10^{10} \times 10) \sim 10^3$ s^{-1}. The expected rate constant if structure **1** were correct is then about 10^3 s^{-1}. Of course, for structure **1** to be correct for the rate-limiting transition state, the migration of the hydronium ion through the resin matrix would have to be faster than is its migration through aqueous solution. This could be true if structured water in the resin cavities promoted an especially efficient Grotthus conductance of the proton. However, the observed rate constant for proton release is actually $10^{-2.1}$ s^{-1}. This is too slow by a factor of 10^5 for the k_1 process to be rate limiting, i.e., for structure **1** to be correct for the transition state. This discrepancy cannot be due to any special features of the resin, which are already accounted for by the magnitude of the measured pK_a. Structure **1** thus appears to be excluded.

For structure **2** to be correct, the observed rate constant of $10^{-2.1}$ s^{-1} ought to be equal to k_1k_2/k_{-1} in eq 1 and 2. In homogeneous solution, an acid of pK_a 8 will have the corresponding quantity $k_1k_2'/k_{-1} \sim 10^2$ s^{-1} (taking k_{-2}' as 10^{10} M^{-1} s^{-1}). The resin might readily reduce the rate constant for proton migration by a factor of 10^4 (to generate the observed value) by: (a) simple steric obstruction to motion,[5,6] (b) the effect of interaction of the migrating ion with ions and dipoles in the resin matrix, and (c) the production of a water structure perhaps unfavorable for proton motion within hydrophobic regions of the resin. Thus structure **2** can readily be reconciled with the magnitude of the rate constant.

If structure **2** is correct, a number of features of the solvent isotope effect[7-13] are predicted. The reactant structure (left-hand side of eq 1) is such that all isotopic fractionation factors[7] $\phi^R = 1$. The transition state **2** contains three hydrogenic sites, all with hydronium-like fractionation factors[7] $\phi_i^T = 0.69$. Therefore the rate constant k_n in an aqueous solvent with atom fraction n of deuterium should be given by eq 6.

$$k_n = k_0(1 - n + 0.69n)^3 \qquad (6)$$

This is a cubic equation and the solid line of Figure 2 is the best-fit cubic representation of the data as determined by polynomial regression.[14] Application of the F test[15] shows the linear and quadratic terms of the representation to be significant beyond the 99.9% confidence level but the cubic term not significant at the 80% level. Thus the solvent isotope effect must arise from more than one transition-state site, but three sites are not statistically required.

A simpler if less rigorous test of the consistency of the data with structure **2** is provided by eq 7 and Figure 3. In eq 7 the cube root in eq 6 is taken, to show that $(k_n/k_0)^{1/3}$ should be linear in n with a slope of $(-1 + 0.69) = -0.31$ if structure **2** is correct.

$$(k_n/k_0)^{1/3} = 1 - n + 0.69n \qquad (7)$$

The slope of the best-fit straight line drawn in Figure 3 is -0.30 ± 0.02. The data are therefore in full consistency with structure **2** for the rate-limiting transition state for ion exchange. It is worth noting that the overall kinetic solvent isotope effects of 3.06 ± 0.17 (Na$^+$) and 3.36 ± 0.38 (K$^+$) are in excellent agreement with the prediction of eq 6 ($k_1/k_0 = [0.69]^3 = 1/3.04$) as well as being identical with the solvent isotope effect for full formation of hydronium ion from many carboxylic acids in homogeneous solution.[16]

We conclude that the transition state for metal-ion-induced proton release from Amberlite CG-50 resin is that of structure **2**, for migration of a preformed hydronium ion though and out of the matrix. In a rapid subsequent step, the metal ion must "trap" the hole created by loss of the hydronium ion.

Experimental Section

Materials. Amberlite CG-50 is an acrylic acid-divinylbenzene copolymer obtained from Mallinckrodt Chemical Co. and was used as received. The metal chlorides were used without any further purification since they were analytical grade, lithium chloride being obtained from Fisher Scientific Co., sodium chloride from J. T. Baker Chemical Co., and potassium chloride from Mallinckrodt. Water was deionized distilled water. Deuterium oxide was purchased from Stohler Isotope Chemicals and was distilled before use.

Solutions. The solutions were prepared as follows. The necessary amount of salt was added to an empty 25-mL volumetric flask. The necessary amount of deuterium oxide was then added by syringe and the weight of the flask plus salt was substracted. Protium oxide was finally added to make up a total volume of 25 mL and its weight was determined.

Titration of the Resin. The potentiometric titration was performed as suggested by Samuelson.[16] Resin (0.1 g) and 10 mL of distilled water were placed in the thermally controlled cell of a Radiometer pH-Stat. From a 10-mL buret, small amounts of 0.1000 N sodium hydroxide were added and the pH of the solution was recorded. The pH vs. volume of sodium hydroxide curve was fitted to a polynomial[13] and the second derivative was obtained analytically. The overall pK_a value was 8.

Kinetic Measurements. Dry resin (0.2 g) was put in the pH-Stat cell which already contained 15 mL of the salt solution thermostated at 25.0 °C. The propeller was switched on after about 1 min. The decrease of the "solution" pH was recorded at different time intervals. The early data (first minute, or around 2 min in heavy water) are not meaningful since many complex processes occur, including exchange at the surface of the resin particle, swelling, etc. The pH-time data after this initial period were converted to concentration-time data and first order plots were constructed. Rate constants were calculated by a non-linear least-squares method. The stirring rate was regulated by adjusting the rubber belt which links the motor and the stirrer into its three different positions. For experiments in isotopic waters, the pH data were converted to concentrations using the glass-electrode correction given by Schowen.[11]

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On the Thermal Rearrangement of Methylenecyclobutane. An Exploration of the Potential Surface[1]

Wolfgang W. Schoeller*

Contribution from the Abteilung für Chemie der Universität, 463 Bochum, West Germany.

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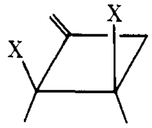
Abstract: An exploration of the potential surface for the thermal reaction of methylenecyclobutane is evaluated by the semiempirical MINDO/2 method and with inclusion of 3 × 3 configuration interaction between the ground state and single and double excited states. The optimization of structures in the transition state region of the hypersurface was carried out in 17 dimensions. The reaction proceeds through a biradical transition state with a flat energy profile. An energy analysis for the midpoint geometries casts doubt on the importance of electronic factors such as those described by Woodward and Hoffmann or Berson and Salem. According to a correlation diagram, quantitatively supported by the calculations, subjacent molecular orbital interaction in this 1,3-sigmatropic (nonpolar) reaction is symmetry allowed for a biradical triplet and symmetry forbidden for a biradical singlet. The quantum chemical study favors the recently given mechanistic interpretation of Gajewski: (a) a ring-opening pathway similar to that of other cyclobutane derivatives; (b) a flat energy profile in the transition state region.

The rules of orbital symmetry by Woodward and Hoffmann[2] have been a milestone in the development of theories about reaction mechanism. According to these rules, a 1,3-sigmatropic reaction should occur either with inversion of configuration at the migrating carbon center and including suprafacial participation of the allyl unit (is) or with retention of configuration at the migrating carbon center and including antarafacial participation of the allyl unit (ra).

However, only a few examples of 1,3-sigmatropic carbon shifts follow closely the concept set by the rules of orbital symmetry.[3] One reaction, presently poorly understood, is the thermal rearrangement of methylenecyclobutane. First predicted by Chesick[4] as automerization, it has been investigated in more detail by Doering and Gilbert,[5] by Doering and Fossel,[6] and by Baldwin and Fleming.[7] From the thermochemical data in comparison with the measured activation energy, one can conclude[5] that the reaction proceeds through a biradical transition state. Thus an aromatic transition state according to Dewar and Evans[8] can be excluded from these considerations.

The reaction is stereoselective: Doering and Fossel observed in the thermal rearrangement of **1** predominant retention of configuration at the migrating carbon center the outcome of stereochemistry in the products to be pressure dependent. Reduction of pressure in the gas phase pyrolysis to 1 mm alters the ratio[9] retention/inversion from 87/13 to 72/28. Baldwin and Fleming concluded from their experimental investigations that at least 77% of the reaction occurs with stereochemistry appropriate to an orbital symmetry allowed reaction,[10] including retention of configuration at the migrating carbon atom and antarafacial participation of the allyl unit. The same experimental observations have been recast recently by Gajewski[12] through a different mechanism. He concludes that the reaction occurs with 100% suprafacial participation of the allyl unit, partially with randomization of the migrating carbon stereochemistry. Therefore the interpretations of the mechanism for this reaction are divergent.



1, X = CO_2CH_3

The experimental observation that a 1,3-sigmatropic reaction can occur in contradiction with the requirements of orbital symmetry according to Woodward and Hoffmann has led Berson and Salem[13] to an important conclusion about the reversal of stereochemistry in 1,3-sigmatropic reactions. Their findings involve interaction of the p atomic orbital at the mi-

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* Address correspondence to this author at Fakultät für Chemie der Universität, 48 Bielefeld, West Germany.