Selective Measurements of Pion Transfer Processes in Alcohols and Carboxylic Acids Using Deuterated Compounds

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Negative pion transfer from pionic hydrogen to carbon and oxygen in alcohols and carboxylic acids was studied. The pion capture probability on hydrogen at a particular site in the molecules was obtained from measurements for the ordinary compound and the deuterated one. The method revealed that the pionic hydrogen atoms originating from hydrogen in different chemical environments show different behavior. The transfer process was discussed with a large mesomolecular model combined with an external transfer process.

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The mechanism of molecular and atomic capture of negative pions has not yet been completely understood, especially in hydrogen-containing molecules. The transfer of pions captured by hydrogen to other atoms complicates the overall process and makes the mechanism hard to understand [1–6]. Most studies have recently been devoted to understanding the transfer process and establishing a capture model which involves the capture process and the successive π^- transfer [7–13].

The π^- transfer is significant in investigating the relation between the chemical state of the Z-H bond and the isolation of pionic hydrogen $(\pi^- p)$ from the bond, because transfer is considered to occur only from an excited $\pi^- p$ atom. An isolated $\pi^- p$ may transfer the π^- to a higher-Z atom in a subsequent collision: $\pi^- p + Z \rightarrow \pi^- Z + p$. The process is called "external transfer" if the π^- is transferred outside the molecule where it was originally captured. The process is "internal transfer" if this occurs in the same molecule. A similar phenomenon may proceed by π^- tunneling along the Z-H bond [7–10].

In the analysis of the pion capture process, the main problem is the fact that the capture probability for a particular Z atom is given as an average over the chemically different states of the same element in the molecule. Observation of the pion capture probability on a particular atom in the molecule, if possible, will give significant information for understanding the pion capture mechanism.

In this study, we try to extract the capture rate for a particular hydrogen atom using deuterated compounds. The capture events by hydrogen undergoing no transfer can be measured by means of a pair of the annihilation γ rays of π^0 produced by the reaction, $\pi^- p \rightarrow \pi^0 n$. To the contrary, the charge-exchange reaction in a $\pi^- d$ atom is strongly suppressed ($\sim 10^{-4}$ [14]). The measurement for deuterated molecules therefore provides the capture probability for hydrogen except for hydrogen at the deuterated site. Thus we can measure selectively the capture rate for a particular hydrogen atom with a comparison between the ordinary compound and the deuterated one.

We selected a series of alcohols, carboxylic acids, and the corresponding compounds with a deuterated hydroxyl or carboxyl group to study the behavior of the $\pi^- p$ atoms originating from hydrogen in different chemical states. Preliminary results for alcohols have been reported [13]. We report here the results for carboxylic acids and the improved results for alcohols, together with a new finding that the behavior of the $\pi^- p$ from the hydrogen bound to oxygen is different between alcohols and carboxylic acids. The chemical effects in the transfer process are discussed based on a combined model [15] which involves a large mesomolecular (LMM) model [1,3,4] and external transfer [2,4].

The samples measured were n-alcohols R-OH and R-OD ($R = C_nH_{2n+1}$, $n = 1$–5) and n-carboxylic acids R-COOH and R-COOD ($R = C_{n-1}H_{2n-1}$, $n = 2$–$4, 6, 8$). The deuterated compounds were prepared by an isotope exchange with D_2O for $C_5H_{11}OD$ and by a D_2O hydrolysis of acid anhydrides for R-COOD ($n = 3, 4, 6, 8$). Commercial reagents were used for the measurements of the other compounds. The water content was determined using the Fischer method after dehydration by molecular sieves, and was found to be less than 0.3% for all samples. The deuterium atomic purity was 97% to 99.5% from a ^{1}H-NMR measurement.

The measurements were performed at the $\pi\mu$ channel of the 12-GeV proton synchrotron in the National Laboratory for High Energy Physics (KEK) [16]. The pionic x rays were measured with two Ge detectors, and the π^0 decays ($\pi^0 \rightarrow 2\gamma$) were detected with a pair of lead glass

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TABLE I. Pion-capture probabilities for the constituent elements and the results of the selective measurement for hydrogen.

			W_H (%)		
Compound	W_C (%)[a]	W_O (%)[a]	W_H	W_H^C [$=W_H$(D)]	W_H^O [$=W_H - W_H$(D)]
CH_3OH(D)	48.9 ± 1.0	50.6 ± 0.5	0.714 ± 0.008	0.626 ± 0.009	0.091 ± 0.012
C_2H_5OH(D)	61.6 ± 1.5	37.6 ± 0.6	0.886 ± 0.011	0.786 ± 0.012	0.100 ± 0.016
C_3H_7OH(D)	71.9 ± 1.6	27.1 ± 0.5	0.998 ± 0.010	0.920 ± 0.009	0.078 ± 0.013
C_4H_9OH(D)	77.2 ± 1.3	21.7 ± 0.5	1.053 ± 0.014	0.978 ± 0.010	0.075 ± 0.017
$C_5H_{11}OH$(D)	80.6 ± 2.5	18.3 ± 0.5	1.075 ± 0.010	1.014 ± 0.011	0.061 ± 0.015
CH_3COOH(D)	42.3 ± 1.1	57.5 ± 1.3	0.218 ± 0.003	0.191 ± 0.004	0.027 ± 0.005
C_2H_5COOH(D)	55.0 ± 1.3	44.7 ± 1.1	0.366 ± 0.004	0.342 ± 0.005	0.024 ± 0.007
C_3H_7COOH(D)	62.9 ± 1.7	36.7 ± 0.9	0.474 ± 0.005	0.464 ± 0.006	0.010 ± 0.008
$C_5H_{11}COOH$(D)	72.6 ± 1.7	26.7 ± 0.7	0.633 ± 0.005	0.626 ± 0.006	0.007 ± 0.008
$C_7H_{15}COOH$(D)	77.9 ± 1.8	21.3 ± 0.6	0.730 ± 0.011	0.729 ± 0.006	0.002 ± 0.013
Syst. err. (%)[b]	6.2	5.4	5.5	5.5	5.5

[a] The attached errors do not include the errors of the x-ray yields.

[b] The systematic errors were estimated according to [15].

Cherenkov counter arrays. Each sample was measured for 4–8 h with a slow π^- beam at 5×10^4 π^-/sec in helium atmosphere to avoid disturbance from air. The experimental method has been described in detail elsewhere [15,17].

The capture probabilities W_O for oxygen and W_C for carbon were obtained from the pionic x-ray intensities and the x-ray yields per captured pion, and shown in Table I. X-ray yields for a single substance cannot be available in the analysis for molecules, because the x-ray intensity pattern and the x-ray yields vary with the chemical environment. The x-ray yields of the (3-2) transition for carbon and oxygen were then deduced from our own data to maintain the consistency between the x-ray intensities and the capture rates for all compounds studied [15]. The capture probability W_H on hydrogen was obtained from the number of π^0 events for the sample by normalization to the number for polyethylene [12]. W_H(D) for the deuterated compounds was corrected for the contribution of the π^- transfer from hydrogen to deuterium using the transfer parameters in the $H_2O + D_2O$ system [18]. The corrected W_H(D) values are also listed in Table I.

The capture probabilities of the hydrogen bound to carbon, W_H^C, corresponds to the W_H(D) values, because the π^0 decay is attributed only to the hydrogen of the alkyl group. The capture probability of the hydrogen bound to oxygen, W_H^O, can be derived from $W_H - W_H$(D). Figures 1 and 2 show the variation in the capture per atom ratios, R_H^C/R_C and R_H^O/R_O, respectively, with the number (n) of carbon atoms in the molecules. The variation should be constant if the π^- transfer occurs only for the atom bonding to the hydrogen in the molecule. Recently, Harston *et al.* explained the change in W_H in a series of alcohols by considering only the transfer to the neighboring atom [12]. However, our results show that the external transfer cannot be neglected in the capture process, as shown in Fig. 1.

The similarity between the variations in R_H^C/R_C and R_H^O/R_O in alcohols also supports the view that the change observed in W_H is attributed to external transfer. The R_H^C/R_C for carboxylic acids shows a tendency similar to that for alcohols. However, Fig. 2 apparently exhibits that $\pi^- p$ atoms from a carboxylic group show different behavior from that for a hydroxyl group. This is a new finding revealed by the selective measurement of W_H.

In a recent report [15], we have tried to combine the modified (LMM) model [19,20] with a phenomenological treatment for external transfer [2]. The following parameters are included in the new model: Λ_Z for the external transfer rate, a'_γ for the isolation process of a $\pi^- p$ atom from the Z-H bond, and σ for the ionicity of the Z-H bond. For compounds consisting of three or more elements, as in the present case, the capture probability $(W')_Z^{Z'}$ within two elements that bound each other, Z-Z', is the object to analyze, and the electron displacement between the

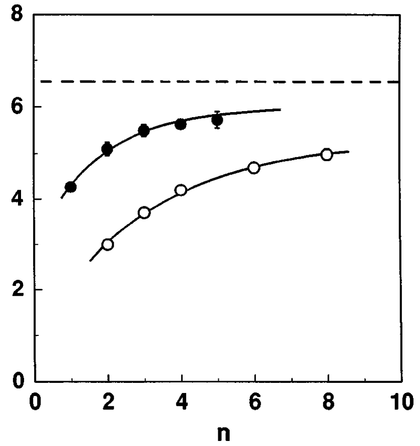

FIG. 1. Capture ratios per atom of the hydrogen bound to carbon relative to the carbon, R_H^C/R_C, as a function of the number (n) of carbon atoms for alcohols (●) and carboxylic acids (○). The dashed line represents the capture ratio for polyethylene. Solid curves are the model calculations with the obtained parameters (see text).

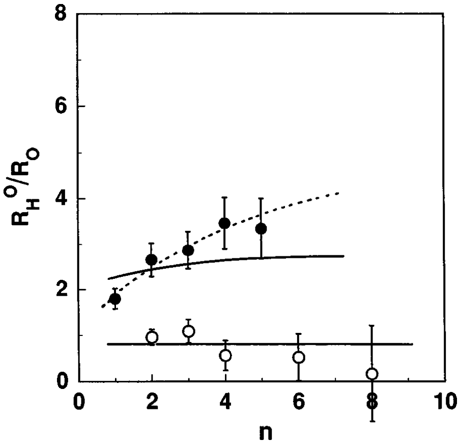

FIG. 2. Capture ratios per atom of the hydrogen bound to oxygen relative to the oxygen, R_H^O/R_O, as a function of the number (n) of carbon atoms for alcohols (●) and carboxylic acids (○). The solid curve represents the model calculations with $\Lambda_C = 1.7$ and $\Lambda_O = 4.1$, and the dotted curve represents those with $a'_\lambda = 0.14$ (see text) for alcohols. No external transfer was found for caroboxylic acids.

relevant atoms is adjusted so as to reproduce each capture probability for each combination of the constituent elements. Here, we considered the following three combinations, $(W')_O^C$ [$=W_O/(W_O + W_C)$], $(W')_H^C$ [$=W_H^C/(W_H^C + W_C)$], and $(W')_H^O$ [$=W_H^O/(W_H^O + W_O)$]. $(W')_O^C$ was calculated according to [18], and $(W')_H^C$ and $(W')_H^O$ were analyzed using a treatment similar to that in Eqs. (5) and (6) in [15]. Only the results of the analysis are presented here.

As for the $(W')_O^C$ values, the model analysis provided the best fit to the experimental data under the condition $\sigma = 0$ for both alcohols and carboxylic acids. The condition is consistent with the chemical nature of the C-O bond.

From the analysis for the $(W')_H^C$ values under the condition of $\sigma = 0$ (the covalent bonding of C-H), we obtained $a'_\gamma = 0.146 \pm 0.006$ and $\Lambda_O = 4.1 \pm 0.5$ for alcohols, and $a'_\gamma = 0.144 \pm 0.007$ and $\Lambda_O = 4.8 \pm 0.5$ for carboxylic acids, providing $\Lambda_C = 1.7 \pm 0.2$ [15]. A noticeable fact supporting the validity of this model is that the model analysis provided the same a'_γ value within the errors among alkanes [15], alcohols, and carboxylic acids. Comparisons between the present values and the empirical estimates are presented in Table II. The difference between two empirical estimates has been attributed to the fact that the $\pi^- p$ atom isolated from the C-H bond lies in the lower excited state compared with that from the H-H bond [4,23]. The obtained Λ_C value is, additionally, smaller than the latter estimate, and the Λ_O values are comparable to the estimates. Strong hindrance in the transfer to carbon atoms of the alkyl group and a slight difference between Λ_O(OH) and Λ_O(COOH) indicate that the steric hindrance of the bonding hydrogen strongly affects the transfer process. A similar effect has been observed in gas phase experiments [24].

TABLE II. Comparison between the experimental and empirical transfer parameters.

	Present work for W_H^C		Empirical estimates	
	R-OH	R-COOH	$H_2 + X$[a]	$C_nH_m + X$[b]
Λ_C	1.7 ± 0.2*[c]	1.7 ± 0.2*[c]	4.6	2.5
Λ_O(OH)	4.1 ± 0.5*[c]	–	5.6	3.0
Λ_O(COOH)	–	4.8 ± 0.5	5.6	3.0

[a] Based on [21] (X = rare gas).

[b] Based on [4,22] (X = rare gas).

[c] Taken from [15].

In the analysis for $(W')_H^O$ values, we could not obtain a reasonable convergence for three parameters. As for the hydroxyl group, assuming that the $\pi^- p$ atoms show the same behavior as those from an alkyl group (i.e., $\Lambda_C = 1.7$ and $\Lambda_O = 4.1$), we obtained $a'_\gamma = 0.115$ under the condition of $\sigma = 0$; taking $a'_\gamma = 0.140$, we obtained $\Lambda_C \sim 0$ and $\Lambda_O = 10 \pm 2$. These results are shown by the solid and dotted curves, respectively, in Fig. 2. The analysis for the carboxyl group provides $a'_\gamma = 0.017 \pm 0.002$ for $\sigma = 0$ (covalent bonding) or $\sigma = -0.8$ for $a'_\gamma = 0.14$ (the same as that for the alkyl group) under the condition of no transfer ($\Lambda_C = 0$ and $\Lambda_O = 0$). Although the latter is qualitatively consistent with the chemical nature of carboxylic acids, the value corresponds to a too large electron displacement ($+0.9e$).

The mean lifetime of a $\pi^- p$ atom was measured to be $(2.3 \pm 0.6) \times 10^{-12}$ s in liquid hydrogen [25]. The lifetime corresponds to the time from the atomic capture to the nuclear capture. However, the lifetime of the $\pi^- p$ atom isolated from Z-H molecules will be shorter than that and longer than 6×10^{-14} s (the estimated lifetime for the $4s$-atomic level) [26], because the π^- should exist in the low excited atomic state ($n = 6 - 4$) when the $\pi^- p$ atom becomes free from the Z-H bond. Recently, it has been reported that the $\pi^- p$ atom from H_2 has a mean kinetic energy of 1–2 eV [27]. Accordingly, we can estimate the travel length of the $\pi^- p$ atom to be 6×10^{-10} to 2×10^{-8} m, which is strongly affected by the angular momentum and energy states of the pion in the isolated $\pi^- p$ atom. Although the behavior of the long-range $\pi^- p$ atoms can be analyzed in the framework of the present model, in the case of the short-range $\pi^- p$ atoms the transfer will occur mainly for the neighboring atoms and thus will be strongly affected by the molecular structure. The observed differences in the Λ_C and Λ_O values between hydroxyl and carboxyl groups may reflect the behavior of the short-range $\pi^- p$ atoms mentioned above.

In conclusion, we found by using a new method that pionic hydrogen atoms originating from hydrogen in hydroxyl and carboxyl groups show different behavior. The combined LMM model successfully explained the whole capture process involving the external transfer observed in the molecules studied. The chemical effects observed in the transfer process indicated that the steric hindrance of the bonding hydrogen strongly affects the transfer process.

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