dations by the use of photoinduced electron transfer at a wide band gap semiconductor (e.g., TiO_2) are also of interest with respect to the Kolbe electrosynthesis. These subjects are currently being investigated in this laboratory.[16]

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(6) Single-Crystal TiO_2, *001* surface area ~0.5 cm^2 doped under H_2/600 °C/35 min; polished with 0.5-μ alumina, etched 30 s with concentrated HNO_3, rinsed with distilled H_2O, dried in vacuum for ~1 h; electrical contact via silver epoxy cemented Cu wire on the back, protected by silicone adhesive.

(7) The purification of acetonitrile described in S. N. Frank, A. J. Bard, and A. Ledwith, *J. Electrochem. Soc.*, **122**, 898 (1975).

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(10) Prepared by mixing 50 mL of 1.0 M tetrabutylammonium hydroxide in methanol (Southwestern Analytical Chemicals, Inc.) with 3.1 g of glacial acetic acid (Fisher Scientific Co.) and removal of solvent at 60 °C (vacuum) for 2 h followed by drying for 5 days at room temperature and 10^{-4} Torr.

(11) Cyclic voltammetry at a platinum electrode shows E_{pa} = 1.2 V vs. Ag/0.1 M $AgNO_3$, 0.1 M TBAP, ACN for acetate oxidation (scan rate 0.2 V/s).[12]

(12) D. H. Geske, *J. Electroanal. Chem.*, **1**, 502 (1959/60), reported a half-wave potential of +1.58 to 1.63 V vs. SCE under similar conditions.

(13) Reference data for the mass spectrum (rel intensity) of ethane (from "Selected Mass Spectral Data", API, 1972: *m/e* 30 (26%), 29 (21%), 28 (100%), 27 (33%), 26 (26%).

(14) Oxygen was not photogenerated in noticeable quantities; small amounts of methane (as reported in ref 9 as a side product of oxidation on Pt) cannot be excluded (signal at *m/e* 16 showed two spikes).

(15) The gas evolving at the platinum cathode did not show a mass spectrum (range, *m/e* 12–100). There exists little doubt that the reduction of acetate/acetic acid on the low overvoltage Pt electrode yielded hydrogen gas. The overall process in the cell can therefore be rewritten:

$$2CH_3CO_2H \rightarrow CH_3CH_3 + H_2 + 2CO_2$$

(16) The support of this research by the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung (to B.K.) and by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

Bernhard Kraeutler, Allen J. Bard*

Department of Chemistry, the University of Texas at Austin
Austin, Texas 78712

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Catalytic Activity of Nearly Zero-Coordinated Calcium Ion in Fully Ion-Exchanged Calcium-A Zeolite

Sir:

The unit cell of molecular sieve zeolite A has three eight-membered oxygen rings, eight six-membered ones, and twelve four-membered ones. The exchangeable cations in zeolite A can occupy a site near the center of the 8-ring (named α site), that of the 6-ring (β site), or that of 4-ring (γ site). The site selectivities of various cations have been extensively studied.[1] The γ site has weak affinities for all cations. Calcium ion has a strong affinity only for the β site. However, it was found recently that at least one Ca^{2+} per unit cell occupies the α site in Ca_6-A zeolite, and is nearly zero coordinated.[2,3] This Ca^{2+} is expected to have a high catalytic activity, since it is weakly bonded to the 8-ring oxygen and has an unusual coordination. In the present work, this expectation was verified by using Ca_6-A as a catalyst for the isomerization of but-1-ene to *trans*- and *cis*-but-2-enes. This is the first demonstration of chemical effects of the zero-coordination that Seff et al. have found by structural analyses.[3,4]

Table I. Catalytic Activities of (Na,Ca)-A Zeolites for Isomerization Reaction of But-1-ene

Catalyst	Reaction temp, °C	Pressure, Torr	Initial rate of isomn, % min^{-1} g^{-1}
Powder Ca_6-A, No. 1	150	16	3.2
Powder Ca_6-A, No. 2	150	16	3.0
Powder $(Na_{1.8}Ca_{5.1})$-A	150	16	2.4
Powder $(Na_{3.6}Ca_{4.2})$-A	150	17	0.31
Pellet Ca_6-A	150	15	14.5
Pellet $(Na_3Ca_{4.5})$-A	150	15	0.45
Bead Ca_6-A	150	15	3.2
Bead $(Na_3Ca_{4.5})$-A	150	15	0.001
Pellet Ca_6-A	200	15	>50
Pellet $(Na_3Ca_{4.5})$-A	200	13	1.2
Bead Ca_6-A	200	18	10.0
Bead $(Na_3Ca_{4.5})$-A	200	14	0.82

Catalysts of powder form with compositions Ca_6-A, $(Na_{1.8}Ca_{5.1})$-A, and $(Na_{3.6}Ca_{4.2})$-A were prepared by a method described in a previous paper.[2] Ca_6-A catalyst in pellet or bead form was obtained by treating commercial 5A zeolite with a nominal composition $(Na_3Ca_{4.5})$-A repeatedly with a solution of 0.2 N $CaCl_2$ at 85 °C.

The isomerization was carried out at 150 °C and 200 °C in a closed recirculation reaction having a volume of ~1570 mL. The catalyst was evacuated at 380 °C for 8 h prior to the reaction, and discarded after a single use to avoid possible trouble due to the polymerization of butene. The reaction mixture was periodically withdrawn from the system and subjected to gas chromatographic analysis, in which a 6-m column packed with propylene carbonate on Uniport C (Gas-Chro Industry Co.) was operated at 0 °C. But-1-ene was obtained from Takachiho Chemical Co. and purified by passage through zeolite at −78 °C.

Curves for amounts of isomers of butene vs. reaction time are well described by first-order kinetics. Let us represent the activity of a catalyst by the initial slope of such a curve for but-1-ene. Catalytic activities of various samples are tabulated in Table I. This table shows that the Ca_6-A form was always the most active, whatever form the catalyst was in, be it powder, pellet, or bead, and at whatever temperature, 150 or 200 °C.

The concentration of Ca^{2+} on the α site per unit cell, $[Ca/\alpha]$, has been determined to be 1.3 for the present powder-form Ca_6-A.[2] If it is assumed that $[Ca/\alpha]$ in $(Na_{12-2x}Ca_x)$-A is the same as that in $(K_{12-2x}Ca_x)$-A, it is 0.4 and 0.0 for $(Na_{1.8}Ca_{5.1})$-A and $(Na_{3.6}Ca_{4.2})$-A, respectively.[2] This assumption may be justified by the following consideration. Ca^{2+} prefers the β site over other sites, and the α site is an uncomfortable residence for it. All β sites crowd on the surface of the sodalite unit which can be considered the unit block constituting the framework of zeolite A. Hence, only a limited number of Ca^{2+} can reside at β sites, since the uneven charge distribution increases the electrostatic energy of the crystal. In (K,Ca)-A, for instance, its population limit is 4 ions per unit cell.[2] The same limit may exist with (Na,Ca)-A, because the electrostatic energy plays the leading role in limiting the population.

In the above catalysts, the activity increases with increasing $[Ca/\alpha]$, though not linearly. It is considered that the reaction was partially retarded by the slow diffusion of the reaction products through the small zeolitic pores, and hence that the catalytic activity did not increase linearly with the concentration of active centers. This view is supported by a low activation energy (~9 kcal/mol) for pellet 5A and bead Ca_6-A samples.

One might argue that the outstandingly high activity of the pellet form of Ca_6-A could be due to the binder in the pellet, which might have been activated by the ion exchange. However, this may be explained by the fact that the bead-form Ca_6-A, containing the same binder, showed the same activity at 150 °C as that of powder-form Ca_6-A which contained no binder. Thus, it is concluded that the high catalytic activity of Ca_6-A is attributed to Ca^{2+} on the α site.

The powder-, pellet-, and bead-form catalysts exhibited considerably different activities. These may be attributed to their texture or pluggings of the zeolite surfaces, which influence the diffusion of the reactants and products. Hence such results do not affect the above conclusion.

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T. Takaishi*
Institute for Atomic Energy, Rikkyo University
Yokosuka, Japan 240-01

H. Hattori
Department of Chemistry, Hokkaido University
Sapporo, Japan 060

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Studies of Single $^{199}Hg^{II}$ Ion Resonances in the Active Site of Human Carbonic Anhydrase B by Fourier Transform Nuclear Magnetic Resonance

Sir:

We wish to report the first direct observation by NMR of $^{199}Hg^{II}$ resonances from a Hg^{II}-protein complex in solution. The very strong, specific binding of Hg^{II} and organomercurials to many proteins, especially those having exposed sulfhydryl groups, has long been employed to provide heavy atom labels in protein x-ray crystallography.[1] The powerful enzyme-inhibiting properties of mercury and its compounds accounts for their well-known toxicities to all living organisms.[2] In the present work we have substituted $^{199}Hg^{II}$ for the naturally occuring Zn^{II} in the active site of the zinc metalloenzyme human carbonic anhydrase B (carbonate hydro-lyase EC 4.2.1.1).[3]

Hg^{II} binds more tightly to HCAB than any other metal ion, but has failed to restore significant activity to carbonic anhydrases under conditions employed to now.[4] Nevertheless, the spin quantum number, $I = 1/2$ and extremely large chemical shift range of known ^{199}Hg compounds (>2500 ppm)[5-7] makes ^{199}Hg interesting as a possible spectroscopic probe of the active site. Furthermore, in conjunction with ^{113}Cd ($I = 1/2$) NMR studies of zinc enzymes,[8] we may obtain useful extrapolations among the d^{10} metal ions to the properties of the zinc enzyme, which has no common Zn isotope with favorable nuclear spin for NMR studies.

Figure 1A shows the ^{199}Hg NMR spectrum[9] at 25 °C of ~4 mL of 7 mM aqueous $^{199}Hg^{II}HCAB$[10] in 0.05 M Tris acetate buffer at pH 7.7. A single, broad (~400 Hz) peak centered at −1310 ppm upfield of neat $(CH_3)_2Hg$ is consistently observed under various sweepwidth and spectrometer offset conditions. The peak broadness in $^{199}Hg^{II}HCAB$ is analogous to our results for uninhibited $^{113}Cd^{II}HCAB$,[8b] and suggests that both

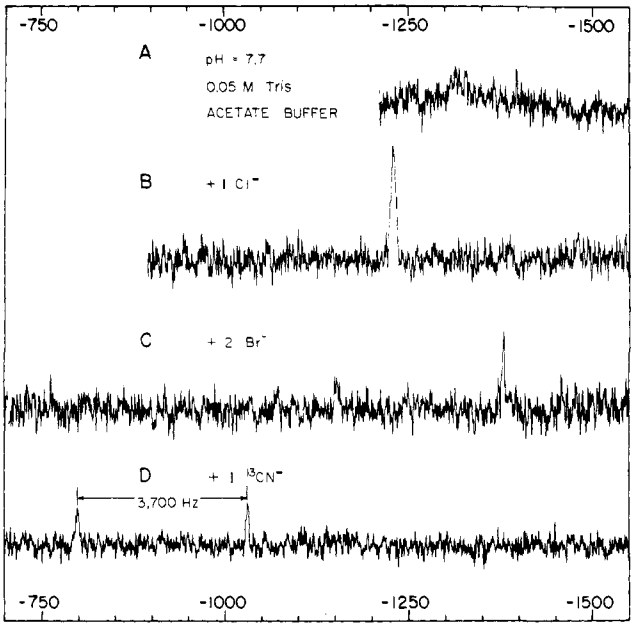

Figure 1. ^{199}Hg FTNMR proton-coupled spectra at 25 °C of 83.5% isotopically enriched 7 mM $^{199}Hg^{II}HCAB$ in 50 mM aqueous Tris acetate, pH 7.7. Chemical shifts (parts per million) are relative to neat $(CH_3)_2Hg$. Exponential multiplication yielding 10-Hz line broadening was applied to the free-induction decays. All spectra are 12-h accumulations: (A) original sample, (B) sample A plus 1 equiv of NaCl, (C) sample B plus 2 equiv of NaBr, (D) sample B plus 1 equiv of $K^{13}CN$ (90% isotopically enriched).

metals undergo ligand-ligand exchange processes at intermediate rates on the NMR time scale. The fact that the Hg^{II} ion occupies the active site of HCAB (rather than the partly accessible sulfhydryl group)[3b] when equimolar Hg^{II} is adduced from the failure of Zn^{II} to restore significant activity.[11]

Figure 1B shows the dramatic change in the ^{199}Hg spectrum caused by addition of 1 equiv of NaCl, analogous to the changes in ^{113}Cd NMR spectra of $^{113}Cd^{II}HCAB$.[8b] The ^{199}Hg resonance shifts downfield (to −1220 ppm) and sharpens to a line width of ~110 Hz or less (sometimes as sharp as ~60 Hz). Evidently Cl^- is strongly bound to or near Hg^{II} in the active site, interrupting the ligand-ligand exchange process. Addition of three equivalents of $NaHCO_3$ has no effect on the spectrum shown in 1B

Figure 1C shows the effect of adding 2 equiv of NaBr to the sample giving rise to Figure 1B. Br^- appears to displace Cl^-, as is also the case in the Cd^{II}[12] and native Zn^{II}[3a] enzymes. The peak at −1380 ppm has a line width of ~50 Hz. In $Cd^{II}HCAB$ containing one Br^- we have evidence[12] for two distinct ^{113}Cd resonances of unequal areas in slow exchange, probably indicating inner sphere and outer sphere binding of Br^-. It is tempting to draw a similar conclusion for $Hg^{II}HCAB$ from the small peak at ~1150 ppm, but until a better signal-to-noise ratio is obtained we reserve judgement.

Figure 1D results from addition of 1 equiv of $K^{13}CN$ (≤90% isotopic enrichment, Merck and Co.). The doublet centered at −910 ppm with a separation of $J_{HgC} = 3700$ Hz and a line width of ~70 Hz indicates direct Hg-C binding. Addition of an additional 3 equiv of $K^{13}CN$ produced no change in the splitting pattern, although J_{HgC} decreased by 40 Hz, presumeably through ionic strength or other medium effects. The tendency of Hg^{II} to bind only one CN^- under these conditions, like the analogous result in $Cd^{II}HCAB$, is surprising in view of its larger ionic radius and consequent displacement (~0.6 Å) away from the three histidyl ligands, at least in crystalline HCAC.[3c]

Preliminary results with ^{15}N-enriched ethylenediamine (en) dihydrochloride indicate that en cannot displace Cl^- from the