spin systems as normalized for a spin of $\frac{5}{2}$, with $g = 2.0$. The fitted exchange parameter is $-0.65 \pm 0.05$ K, and a molecular field correction to account for interchain interactions takes the value $zJ/k = -0.46 \pm 0.05$ K. Several equally good fits can be obtained by varying $J/k$ in one direction and then compensating by a change in the value of $zJ/k$. These values combine to yield an average value of $J/k + zJ/k \approx -1.76$ K, which may be compared to the value $-1.97$ K obtained in the following fashion. The relationship $\chi_{\perp}(0) = N g^2 \mu_B^2 / 4 |zJ|$ is obtained from both molecular field and spin-wave theories, where $\chi_{\perp}(0)$ is the perpendicular susceptibility in the ordered state, extrapolated to 0 K. For $\text{Cs}_2\text{FeCl}_3\cdot\text{H}_2\text{O}$, our data along the $b$ and $c$ axes suggest $\chi_{\perp}(0) = 0.19$ emu/mol, which leads to the value of $zJ/k$ given above. Zero-point spin deviations should decrease the experimental value of $\chi_{\perp}(0)$ by some 5% for $S = \frac{5}{2}$, causing the exchange constant evaluated in this way to be too large. As with $\text{MnCl}_2\cdot\text{H}_2\text{O}$, the influence of the exchange constant $J$ is much more significant than that of the chloride analogue, causing the usual broad maximum anticipated in the susceptibilities of a chain magnet to be obscured.

On the other hand, a sharp $\lambda$ peak at 6.57 $\pm$ 0.05 K is observed (Figure 2) in the specific heat of $\text{Cs}_2\text{FeCl}_3\cdot\text{H}_2\text{O}$, but none of the usual features expected for linear chain magnets are apparent. The measured critical temperatures agree within experimental error. The lattice heat capacity has been evaluated tentatively by an empirical procedure. The magnetic contribution to the heat capacity was evaluated by difference, and allowed an estimate of the magnetic entropy. A value of $\Delta S = R \ln (2S + 1) = 3.56$ cal/mole-K is calculated for iron-(III) systems, and $\Delta S = 3.65$ cal/mole-K was determined in the case of $\text{Cs}_2\text{FeCl}_3\cdot\text{H}_2\text{O}$. One is forced to conclude that the assignment of one-dimensional character from the susceptibility results is more extreme than the true situation.

The parameters describing the other members of the series are included in Table I. The high transition temperatures cause considerable difficulty in an analysis in terms of magnetic model systems, and the other exchange parameters provided must be considered only as suggestive at this time. With the possible exception of the ferromagnetic $\text{A}_2\text{CuX}_2\cdot\text{H}_2\text{O}$ series, this set of iron compounds (along with the ammonium and potassium analogues) appears to be the largest series of isostructural ordered magnets currently known. A careful analysis of the heat capacity results is in progress, and the degree of anisotropy present can be best derived from the magnetic phase diagram. It is of interest to note that, for a given alkali ion, $T_c$ for a bromide compound is always higher than that of the chloride analogue. While that is behavior characteristic of many such isomorphous pairs of hydrated halides, what is novel in these results is the discovery of the $T_c$ dependence upon the alkali ion, A. Since superexchange interactions are known to have approximately an $r^{-12}$ dependence between metal ion centers, a complete crystal structure analysis of each member of this series is required before a rationalization can be provided for this result.

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**References and Notes**

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(9) L. J. de Jongh, W. D. van Amstel, and A. R. Miedema, Physica (Utrecht), 58, 277 (1972), for a discussion of this point.
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(17) Department of Chemistry, University of Virginia, Charlottesville, Va. 22901.

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**Photoelectrosynthesis of Ethane from Acetone Ion at an n-Type TiO2 Electrode. The Photo-Kolbe Reaction**

**Sir,**

Most of the recent interest in semiconductor electrodes has been concerned with their application to photovoltaic cells and to the photoelectrolysis of water to hydrogen and oxygen. Although some studies of the electrochemical behavior of organic substances at semiconductor electrodes have been reported, little attention has been paid to photoassisted synthesis at semiconductor electrodes (photoelectrosynthesis). We thought it of interest to extend these studies to a classical electrochemical synthetic reaction, the oxidation of carboxylates (the Kolbe reaction), and report here the photoassisted oxidation of acetate ion to ethane in acetonitrile (ACN) solutions at n-type TiO2 electrodes in both the single-crystal and chemically vapor deposited polycrystalline form. This reaction is of interest because it should provide a means of using solar energy to synthesize hydrocarbons directly from inorganic compounds.

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energy to produce hydrocarbons via the widely studied Kolbe reaction.

The reaction typically was carried out in a vacuum-tight one-compartment Pyrex cell which was fitted with a flat window. The cell was equipped with single-crystal n-type TiO$_2$ and platinum disk working electrodes, a platinum (wire or foil) counter electrode, and a silver wire reference electrode. Acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) was used as the reaction medium to minimize competition due to solvent oxidation. This reaction medium was shown by Russell and Ansong to be suitable for a clean competition due to solvent oxidation. This reaction medium was shown by Russell and Ansong to be suitable for a clean competition due to solvent oxidation. 

The reaction mechanism thus follows that for other photoassisted oxidations at n-TiO$_2$. Light of energy greater than $E_g$ causes formation of electron-hole pairs. When the potential of the semiconductor is positive of the flat-band potential, the bands are bent upward and the photogenerated holes ($p^+$) migrate to the electrode surface while the electrons drift to the bulk of the electrode, thus preventing recombination. The holes, at energies characteristic of the valence band or low lying surface states, are effectively strong oxidizing agents and can abstract electrons from acetate ions initiating the cascade of steps in the Kolbe reaction:

$$\text{CH}_3\text{CO}_2^- + p^+ \rightarrow \text{CH}_3\text{Y} \rightarrow \text{CO}_2$$  \hspace{1cm} (1) \\
$$2\text{CH}_3\text{Y} \rightarrow \text{C}_2\text{H}_6$$ \hspace{1cm} (2)

Since the photo-Kolbe reaction occurs at potentials $\sim$2.4 V more negative than those for the oxidation at platinum, the effective efficiency of utilization of the excitation energy is high. The chemical irreversibility of the overall process prevents back donation of electrons from the electrode and leads to an overall high efficiency for the process. The potential for the photooxidation of acetate is negative of that for the onset of hydrogen ion reduction in the acetate/acetic acid mixture (ca. −0.8 V vs. Ag-wire reference), suggesting that photoelectrolysis with little or no external applied voltage leading to a mixture of ethane and hydrogen is possible. Furthermore the control of current density via the light flux and the possible suppression of undesirable two-electron oxid-
Catalytic Activity of Nearly Zero-Coordination 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 for the β site. However, it was found recently that at least one Ca2+ per unit cell occupies the α site in Ca6-A zeolite, and is nearly zero coordinated.2,3 This Ca2+ 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 Ca6-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.4

Catalysts of powder form with compositions Ca6-A, (Na3Ca5,1)-A, and (Na3,6Ca4,2)-A were prepared by a method described in a previous paper.2 Ca6-A catalyst in pellet or bead form was obtained by treating commercial 5Å zeolite with a nominal composition (Na8Ca4,5)-A repeatedly with a solution of 0.2 N CaCl2 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-ft column packed with propylene carbonate on Unipor 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 Ca6-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 Ca2+ on the α site per unit cell, [Ca/α], has been determined to be 1.3 for the present powder-form Ca6-A.2 If it is assumed that [Ca/α] in (Na12,2Ca3)-A is the same as that in (K12,2Ca3)-A, it is 0.4 and 0.0 for (Na3Ca5,1)-A and (Na3,6Ca4,2)-A, respectively.2 This assumption may be justified by the following consideration. Ca2+ prefers the sodalite unit which can be considered the unit block constituting the framework of zeolite A. Hence, only a limited number of Ca2+ can reside at β sites, since the uneven charge distribution increases the electrostatic energy of the crystal. In (K,Na)-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.

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction temp., °C</th>
<th>Pressure, Torr</th>
<th>Initial rate of isomn, % min⁻¹ g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Ca6-A, No. 1</td>
<td>150</td>
<td>16</td>
<td>3.2</td>
</tr>
<tr>
<td>Powder Ca6-A, No. 2</td>
<td>150</td>
<td>16</td>
<td>3.0</td>
</tr>
<tr>
<td>Powder (Na12,2Ca3)-A</td>
<td>150</td>
<td>16</td>
<td>2.4</td>
</tr>
<tr>
<td>Powder (Na3Ca5,1)-A</td>
<td>150</td>
<td>17</td>
<td>0.31</td>
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<tr>
<td>Pellet Ca6-A</td>
<td>150</td>
<td>15</td>
<td>14.5</td>
</tr>
<tr>
<td>Pellet (Na3Ca5,1)-A</td>
<td>150</td>
<td>15</td>
<td>0.45</td>
</tr>
<tr>
<td>Bead Ca6-A</td>
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<td>15</td>
<td>3.2</td>
</tr>
<tr>
<td>Bead (Na3Ca5,1)-A</td>
<td>150</td>
<td>15</td>
<td>0.001</td>
</tr>
<tr>
<td>Pellet Ca6-A</td>
<td>200</td>
<td>15</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Pellet (Na3Ca5,1)-A</td>
<td>200</td>
<td>13</td>
<td>1.2</td>
</tr>
<tr>
<td>Bead Ca6-A</td>
<td>200</td>
<td>18</td>
<td>10.0</td>
</tr>
<tr>
<td>Bead (Na3Ca5,1)-A</td>
<td>200</td>
<td>14</td>
<td>0.82</td>
</tr>
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</table>

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