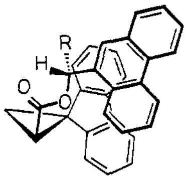
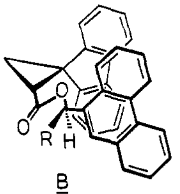
For estimation of the rate of energy transfer from the phenanthryl to the fluorenyl group, the triplet decay of the phenanthryl group in **4Aa–c** and **4Ba–c** was measured by means of flash and laser photolyses. From the observed decay curves, the first- and the second-order rate constants can be distinguished by the concentration dependence of the decay. The first-order rate constants (k_1, Table I[7]) are remarkably different between the diastereomers (k_1(**4Ba–c**)/k_1(**4Aa–c**): 27 for R = Me, 46 for R = Et, 79 for R = *i*-Pr), strongly suggesting that the rate of intramolecular energy transfer from the phenanthryl to the fluorenyl moiety is much faster in **4Ba–c** than in **4Aa–c**. This can be rationalized by the conformational models A and B. Triplet energy transfer, which is widely thought to occur via an electron exchange mechanism, from the phenanthryl to the fluorenyl group requires an orbital overlap[8] of these chromophores. Such an overlap is easily achieved in B but not in A owing to steric repulsion between the alkyl and the fluorenyl groups.[9,10] As a consequence, **4Aa–c** is photochemically less reactive than **4Ba–c**. The second-order decays of the triplet excited states, which are in the range of 1–3 × 10^6 M^{-1} s^{-1} for **4Aa–c** and 10–50 × 10^6 M^{-1}/s^{-1} for **4Ba–c**,[7] are interpreted as intermolecular energy transfers from the phenanthryl to the fluorenyl moiety.



A



B

It is interesting to note from Table I that the photostationary state ratio of **4Aa–c**:**4Ba–c** largely deviates from the ratio expected from the quantum yields of **4Aa–c** and **4Ba–c**. This is due to isoenergetic intermolecular energy transfer between the phenanthryl groups from **4Aa–c**, having the longer triplet life time, to **4Ba–c**, which more rapidly isomerizes to **4Aa–c** after the above mentioned intramolecular energy transfer. As a result, the diastereoselectivity is concentration dependent (Figure 1). The higher the concentration, the higher the stereoselectivity. The intercept (1.8 ± 0.1 for **4A(B)a**, 4.5 ± 0.3 for **4A(B)b**, 5.5 ± 0.9 for **4A(B)c**) at 0 M of the substrate is close to the ratio of quantum yields.

In summary, we have demonstrated that the triplet lifetime of the phenanthryl group of **4Ba–c** is 30–80 times shorter than that of **4Aa–c**. Since these values are large enough to account for the diastereoisomeric ratio at the photostationary state (2–33 at the concentration up to 1.2 × 10^{-3} M which is close to the saturation limit), we conclude that the diastereodifferentiation mainly operates in the energy-transfer step. Large concentration effect on the diastereoselectivity also supports this conclusion. More detailed studies including temperature effects and asymmetric synthesis with use of chiral α-arylalkyl groups will be published in a full paper.

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[7] The second-order rate constants (k_2) are as follows: (k_2 × 10^{-6} M^{-1} s^{-1}) 2.2 ± 1.1 for **4Aa**, 42 ± 13 for **4Ba**, 1.4 ± 0.7 for **4Ab**, 18 ± 5 for **4Bb**, 2.6 ± 1.3 for **4Ac**, 27 ± 8 for **4Bc**. These data suggest that the intramolecular energy transfer from the phenanthryl group to the spirocyclopropanefluorene moiety is endothermic in the extent of 3–5 kcal/mol; triplet energy of spirocyclopropanefluorene moiety will be about 65–67 kcal/mol.

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[10] The ^1H resonance of the methyl protons of **4Aa–c** (δ in $CDCl_3$: 1.51 for **4Aa**, 0.56 for **4Ab**, 0.58 for **4Ac**) appears at higher field than those of **4Ba–c** (δ in $CDCl_3$: 1.74 for **4Ba**, 1.00 for **4Bb**, 0.98 for **4Bc**) supports these conformational models.

"Pseudoliquid" Behavior of Heteropoly Compound Catalysts. Unusual Pressure Dependencies of the Rate and Selectivity for Ethanol Dehydration

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Heteropoly compounds are now utilized as industrial catalysts for olefin hydration and aldehyde oxidation and as interesting cluster models of mixed oxide catalysts.[1]

Certain heteropoly acids, like $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, easily absorb a large amount of water, alcohols, and ethers in the solid state, although their surface areas are very low.[2] This is not adsorption in micropores; rather molecules are absorbed between the lattice polyanions, sometimes expanding the lattice. The expansion can be seen visually as well as by X-ray diffraction. We showed that in some cases catalytic reactions take place in this novel bulk phase.[2,3] Presumably due to this behavior, very high catalytic activity and unique selectivity[4] as well as unusual reactivity order[5] have been observed. We called this state the "pseudoliquid phase". However, in only one case[3] was the amount of absorbed reactant measured under the working conditions.

We report here unusual pressure dependencies of the rate and selectivity of ethanol dehydration over heteropoly compounds. The dependency can only be explained by the formation of a pseudoliquid phase, i.e., a phase where the amount of absorbed ethanol has changed as a function of ethanol pressure.

Reactions were carried out by a conventional flow method, with 0.4–60 kPa of ethanol in He. The outlet gas was directly introduced to a quadrupole mass spectrometer and a gas chromatograph. Catalysts were $H_3PW_{12}O_{40}{\cdot}nH_2O$ (surface area: 5 m^2 g^{-1}) and a typical acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}{\cdot}nH_2O$ (114 m^2 g^{-1}), of which the physical and acidic properties have been described previously.[4] Prior to the reaction, these compounds were pretreated in situ in the stream of He for 1 h at 150 °C. The values of n after this pretreatment was close to zero.[7] It was confirmed that the rate and the composition of the products changed little during the time course of the reaction and that the selectivity was constant up to 60% conversion when the amount of catalyst was increased.

The amount of absorbed ethanol under the working conditions was directly measured by means of a transient-response method as described below.[3] At the stationary state of the reaction, the feed gas was instantaneously changed from ethanol-d_0 to -d_6, and the variation of the composition at the outlet was followed by a mass spectrometer and a gas chromatograph. The content of ethanol-d_0 plus -d_1 (C_2H_5OH and C_2H_5OD) in the outlet gas decreased and the content of C_2D_5OD plus C_2D_5OH increased, but the change occurred more slowly than in an experiment without a catalyst. The differences of these transient responses compared to the blank experiment correspond to the amounts of ethanol being absorbed under the working conditions. From the analysis of the transient-response curve, it can be further shown that the rate of absorption–desorption is much faster than the rate of dehydration.[3]

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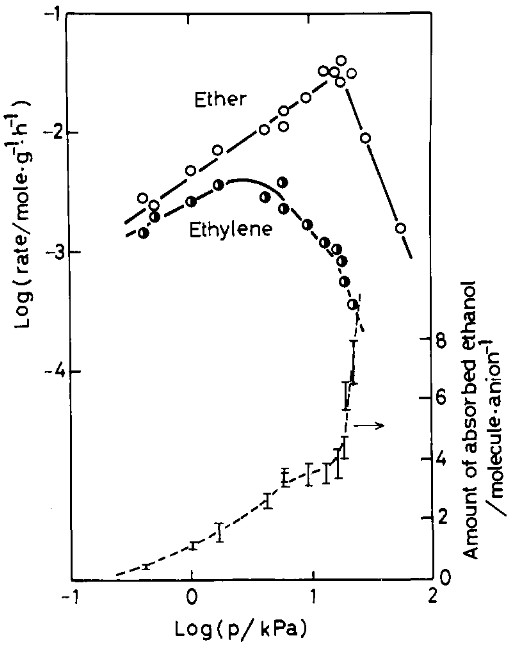

Figure 1. Rates of the formation of diethyl ether and ethylene from ethanol over $H_3PW_{12}O_{40}$ (ethanol basis) as well as the amount of absorbed ethanol under the working conditions as a function of the partial pressure of ethanol. Reaction temperature: 130 °C, W/F (ratio of the catalyst weight to the feed rate): 2-60 g·h·mol^{-1}.

Figure 1 shows the pressure dependencies of the rates of ether and ethylene formation observed for $H_3PW_{12}O_{40}$. The rates increased at first with increasing ethanol pressure (ca. 0.5-0.8th order) but then decreased markedly at higher pressures with the maximum clearly occurring at a higher pressure for the formation of ether. This pressure dependency is quite different from those observed for ordinary solid acids like SiO_2-Al_2O_3 and Al_2O_3; on such solid acids the formation of ethylene is usually zero order and that of ether zero to first order.[6] Moreover, the catalytic activity of $H_3PW_{12}O_{40}$ was 10^2 times greater than SiO_2-Al_2O_3.

The amounts of absorbed ethanol were determined as shown in Figure 1. The amount increased from 0.4 to 8 molecules/anion as the partial pressure of ethanol increased from 0.4 to 60 kPa. These amounts correspond to 4-80 times the monolayer (ca. 20-400 times the number of the surface polyanions), showing that most of the ethanol molecules were absorbed into the bulk. Therefore, it is very likely that the ethanol reaction proceeds mainly in the absorbed phase, just as we showed for dehydration of 2-propanol.[3]

It is also worth noting that the amount of absorbed ethanol varied, apparently corresponding to the changes in the rates. Since ethylene is formed from one molecule of ethanol and ether from two molecules, ethylene may be preferably formed when the ratio of ethanol to protons in the pseudoliquid phase is low, and ether may be favored as the ratio increases. Equations 1 and 2 present a reasonable mechanism. Reactions similar to the first parts of

$$C_2H_5OH + H^+ \overset{K_1}{\rightleftharpoons} C_2H_5OH_2^+ \xrightarrow{k_1} C_2H_4 + H_2O \qquad (1)$$

$$C_2H_5OH + C_2H_5OH_2^+ \overset{K_2}{\rightleftharpoons} (C_2H_5OH)_2H^+ \xrightarrow{k_2} (C_2H_5)_2O + H_2O \qquad (2)$$

eq 1 and 2 occur for pyridine absorbed into a $H_3PW_{12}O_{40}$ lattice: $py + H^+ \rightleftharpoons H^+py$ and $py + H^+py \rightleftharpoons (py)_2H^+$.[7] Since, in the present case, the amount of absorbed ethanol increased sharply at about 15 kPa and was accompanied by a rapid decrease of the reaction rate, a phase change at this pressure to an inactive phase containing too much ethanol is indicated. In other words, $(C_2H_5OH)_nH^+$ ($n \geq 3$) is much less reactive for the formation of both products.

$$C_2H_5OH + (C_2H_5OH)_2H^+ \overset{K_3}{\rightleftharpoons} (C_2H_5OH)_3H^+ \text{ (not reactive)} \qquad (3)$$

According to this model, the concentrations of monomer ($C_2H_5OH_2^+$), dimer ($(C_2H_5OH)_2H^+$), and oligomer increase in first, second, and higher order, respectively, with respect to the ethanol pressure. So this model explains the essential trends found in Figure 1, for example, the maximum rate of ether formation was at a higher partial pressure of ethanol than that for ethylene formation, and the rates for both reactions were low at high ethanol pressures. For example, with K_1, K_2, and K_3 values of 2.3×10^{-4}, 5.3×10^{-4}, and 7.5×10^{-6} Pa^{-1}, respectively, the general trends were fairly well reproduced. Since the absorption-desorption processes are rapid, it is not rate-controlling step. Hence the dehydration can take place homogeneously in the bulk phase. This is the pseudoliquid phase which provides a unique reaction media for organic reactions and also makes spectroscopic studies of catalytic processes very feasible.[7,8]

Further evidence for the pseudoliquid phase is provided by examining $Cs_3PW_{12}O_{40}$. In the case of the Cs salt, only ether was formed on a zero-order reaction. The amount of ethanol absorbed was ca. 0.5 molecules/anion (0.4 times the monolayer) and nearly constant over the pressure range. This behavior corresponds closely to that observed for ordinary solid acids in the limiting case of high partial pressure.[6] The difference between the acid form and the Cs salt is explained by the very different absorptivity of these compounds,[4] and the Cs salt shows no tendency to exhibit a pseudoliquid phase.

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Carboxypeptidase A: Novel Enzyme-Substrate-Product Complex

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As part of our continuing X-ray crystallographic studies of carboxypeptidase A (CPA) and its interaction with inhibitors[1-6] and substrates,[7] we now report the structure of the complex between CPA and the slowly hydrolyzed substrate *N*-benzoyl-L-phenylalanine (BZF).[8,9] More properly, the structure observed at room temperature as well as slightly subzero temperature is that of an enzyme-substrate-product complex. The structure also represents an enzyme-products complex for the hydrolysis of *N*-benzoyl-L-phenylalanine-L-phenylalanine and may depict the

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