[1] S. J. Lippard, J. M. Berg, *Principles of Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, **1994**.
[2] T. E. Creighton, *Proteins: Structures and Molecular Properties*, W. H. Freeman, New York, **1993**.
[3] J. Halpern, B. R. James, A. L. W. Kemp, *J. Am. Chem. Soc.* **1961**, *83*, 4097 – 4098.
[4] V. Janout, S. L. Regen, *J. Org. Chem.* **1982**, *47*, 3331 – 3333.
[5] Y. Fukuda, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 3729 – 3731.
[6] J. Blum, H. Huminer, H. Alper, *J. Mol. Catal.* **1992**, *75*, 153 – 160.
[7] J. W. Hartman, W. C. Hiscox, P. W. Jennings, *J. Org. Chem.* **1993**, *58*, 7613 – 7614.
[8] W. Baidossi, M. Lahav, J. Blum, *J. Org. Chem.* **1997**, *62*, 669 – 672.
[9] T. Tsuchimoto, T. Joya, E. Shirakawa, Y. Kawakami, *Synlett* **2000**, 1777 – 1778.
[10] a) J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, pp. 787 – 788; b) H. Sakurai, M. Ando, N. Kawada, K. Sato, A. Hosomi, *Tetrahedron Lett.* **1986**, *27*, 75 – 76.
[11] C. Bruneau, P. H. Dixneuf, *Acc. Chem. Res.* **1999**, *32*, 311 – 323; for other good leading references to the capabilities of ruthenium complexes to transform alkynes, see also S. Dérien, L. Ropartz, J. Le Path, P. H. Dixneuf, *J. Org. Chem.* **1999**, *64*, 3524 – 3531; C. Slogovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1998**, *17*, 827 – 831; B. M. Trost, R. E. Brown, F. D. Toste, *J. Am. Chem. Soc.* **2000**, *122*, 5877 – 5878.
[12] M. Tokunaga, Y. Wakatsuki, *Angew. Chem.* **1998**, *110*, 3024 – 3027; *Angew. Chem. Int. Ed.* **1998**, *37*, 2867 – 2869.
[13] T. Suzuki, M. Tokunaga, Y. Wakatsuki, *Org. Lett.* **2001**, *3*, 735 – 737.
[14] B. H. Lipshutz, M. C. Morey, *J. Org. Chem.* **1983**, *48*, 3745 – 3750.
[15] C. Hilf, F. Bosold, K. Harms, J. C. Lohrenz, M. Marsch, *Chem. Ber.* **1997**, *130*, 1201 – 1212.
[16] Conditions used were patterned after N. J. Curtis, R. S. Brown, *J. Org. Chem.* **1980**, *45*, 4038 – 4040. For synthesis of several analogs of **2**, see D. B. Grotjahn, D. Lev, Y. Gong, G. Boldt, G. Aguirre, *Organometallics*, manuscript submitted.
[17] D. B. Grotjahn, H. C. Lo, *Organometallics* **1996**, *15*, 2860 – 2862.
[18] For **4** ($C_{46}H_{53}F_3N_4O_4P_2RuS$): monoclinic, $P2_1/n$, $a = 14.517(3)$, $b = 19.349(4)$, $c = 16.900(3)$ Å, $\beta = 98.824(19)^\circ$, $V = 4690.9(15)$ Å^3, $Z = 4$, $Z' = 1$, $T = 251(2)$ K, $\rho_{calcd} = 1.385$ g cm^{-1}, orange block, $GOF = 1.184$, $R(F) = 0.0525$ for 6433 observed independent reflections. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163304. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[19] For examples, see: A. P. Kozikowski, P. D. Stein, *J. Org. Chem.* **1984**, *49*, 2301 – 2309; N. Adjé, P. Breuilles, D. Uguen, *Tetrahedron Lett.* **1993**, *34*, 4631 – 4634; I. Berque, P. Le Ménez, P. Razon, J. Mahuteau, J.-P. Férézou, A. Pancrazi, J. Ardisson, J.-D. Brion, *J. Org. Chem.* **1999**, *64*, 373 – 381.
[20] Y. Nishibayashi, I. Wakiji, M. Hidai, *J. Am. Chem. Soc.* **2000**, *122*, 11 019 – 11 020.
[21] The phosphane P(4-ClC_6H_4)$_3$ models the mild electron-withdrawing character of the imidazole ring compared with phenyl. The electronic effect of the imidazole substituent was probed using *trans*-[Rh(Cl)(CO)(L)$_2$] where L = the *N*-isopropyl analogue of **2** (D. Grotjahn, unpublished results). For this complex $\nu_{CO} = 1982$ cm^{-1} (CH_2Cl_2), whereas for analogous complexes with L = PPh_3 and P(4-ClC_6H_4)$_3$ $\nu_{CO} = 1978$ and 1984 cm^{-1}: A. Huang, J. E. Marcone, K. L. Mason, W. J. Marshall, K. G. Moloy, *Organometallics* **1997**, *16*, 3377 – 3380.
[22] J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, p. 762.
[23] a) C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa, F. Zanobini, *J. Am. Chem. Soc.* **1996**, *118*, 4585 – 4594, and references therein; b) M. I. Bruce, A. G. Swincer, *Aust. J. Chem.* **1980**, *33*, 1471 – 1483; c) M. L. Buil, M. A. Esteruelas, A. M. López, E. Oñate, *Organometallics* **1997**, *16*, 3169 – 3177.
[24] For relevant proposals about the role of an *N*-protonated pyridylphosphane ligand (cf. **F**), see: E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organometal. Chem.* **1994**, *475*, 57 – 63; A. Scrivanti, V. Beghetto, E. Campagna, M. Zanato, U. Matteoli, *Organometallics* **1998**, *17*, 630 – 635; M. T. Reetz, R. Demuth, R. Goddard, *Tetrahedron Lett.* **1998**, *39*, 7089 – 7092.

Metal-Catalyzed Selective Deoxygenation of Diols to Alcohols**

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Design and discovery of new catalysts that operate by nontraditional mechanisms offer the possibility of efficient and selective transformations that are difficult to achieve by conventional methods. Reactions proceeding through ionic mechanisms are attractive targets for development in this context. The traditional homogeneous catalytic hydrogenation of carbonyl groups[1] involves the coordination of a ketone or aldehyde substrate to a metal center and insertion of the C=O bond into a metal hydride bond. In ionic hydrogenations, hydrogen gas is heterolytically cleaved by a metal complex and then added to an unsaturated organic compound through proton (H^+) and hydride (H^-) transfer steps. We recently reported Mo and W catalysts for ketone hydrogenation that operate by an ionic hydrogenation pathway under mild conditions.[2] Magee and Norton discovered a Ru system that catalyzes the enantioface-selective hydrogenation of C=N bonds by an ionic mechanism.[3] Shvo and co-workers reported a remarkable series of reactions catalyzed by ruthenium complexes with phenyl-substituted cyclopentadienone ligands,[4] and recent studies by Casey et al. demonstrated that the proton and hydride transfer are concerted in such systems.[5] The remarkably reactive Ru hydrogenation catalysts of Noyori and co-workers are now thought to proceed by a related mechanism in which H_2 is cleaved to form M–H and N–H bonds.[6]

Synthetic procedures for deoxygenation of alcohols[7] generally involve multiple steps and low atom efficiencies.[8] *Selective* deoxygenation of one of the two OH groups of diols presents an even more formidable challenge than the deoxygenation of alcohols. Vicinal OH functionalities represent a ubiquitous feature of compounds derived from carbohydrates, but diols and polyols are unsuitable precursors for many industrial applications because they are overfunctionalized with an abundance of OH groups of very similar reactivity. Conversion of biomass to useful industrial chemicals[9] offers an attractive solution to consumption of petroleum-based resources, an aspect of growing concern. We

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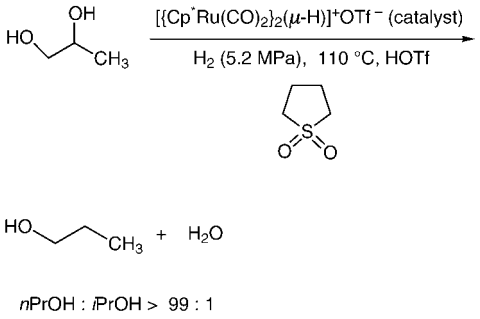
present here a homogeneous catalyst system that achieves the reductive deoxygenation of the model system 1,2-propanediol to *n*-propanol with high regioselectivity.

The ruthenium complex[10] $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+OTf^-$ ($Cp^* = \eta^5\text{-}C_5Me_5$; $OTf = OSO_2CF_3$) catalyzes the reductive deoxygenation of diols to alcohols. The reaction is carried out under hydrogen at 110 °C with added HOTf in sulfolane. Equation (1) shows the catalytic deoxygenation of our model



(1)

compound 1,2-propanediol to *n*-propanol, and Figure 1 depicts the time profile of this reaction. After 6.4 h, the concentration of *n*-propanol was 0.38 M (38 %), and increased

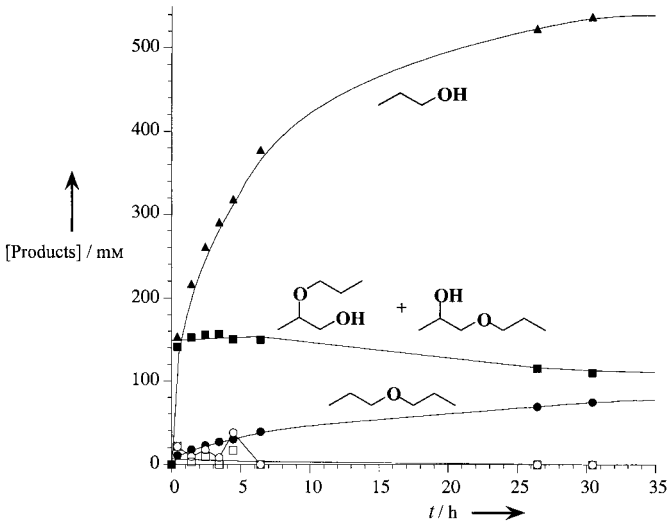
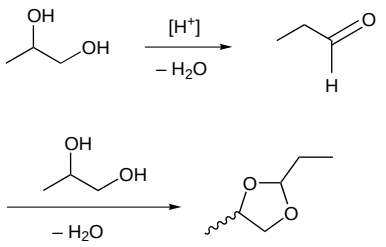


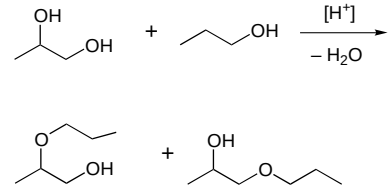
Figure 1. Time profile of products resulting from reaction of 1,2-propanediol. Initial concentrations and reaction conditions were 1.0 M 1,2-propanediol, 5 mM $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+OTf^-$, and 60 mM HOTf under H_2 (5.2 MPa initial pressure before heating) at 110 °C in sulfolane. Final products are shown as solid symbols and are labeled. Intermediates propionaldehyde and 2-ethyl-4-methyl-1,3-dioxolane are shown as open circles and open squares, respectively.

to 0.52 M (52 %) after 26 h. This reaction exhibits a selectivity of >99 % for deoxygenation of the secondary over the primary OH group. Propionaldehyde, which results from acid-catalyzed dehydration of 1,2-propanediol [Eq. (2)], was observed as an intermediate (typically <5 %); its C=O bond is hydrogenated under the reaction conditions to give *n*-propanol. Separate experiments verify that aldehydes and ketones are catalytically hydrogenated to alcohols using $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+$. We suggest that the observed selectivity is largely determined by the regiochemistry of the elimination of water from the protonated diol. Dehydration from the terminal OH group of the diol would be strongly disfavored, particularly if the loss of water more resembled an E1 mechanism than an E2 pathway, with the former being much more sensitive to the stability of the incipient carbenium ion. Another intermediate detected (also typically <5 %) in the deoxygenation reaction was the acetal 2-ethyl-4-methyl-1,3-dioxolane [*cis*/*trans* isomers; Eq. (2)] which results from reaction of propionaldehyde with 1,2-propanediol.



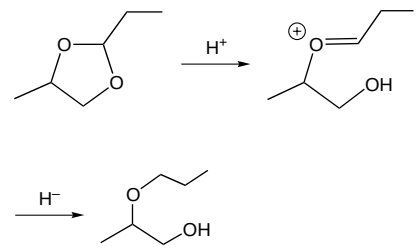
(2)

Additional ether products are observed under the deoxygenation reaction conditions. Cross-condensation of *n*-propanol with 1,2-propanediol would produce two isomers of propylene glycol propyl ether [Eq. (3)], and condensation of



(3)

n-propanol with itself would give di-*n*-propyl ether. Taking into account these ether products along with the *n*-propanol, a total of 160 turnovers (moles of hydrogenation products per mole of $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+$) was observed after 30 h (80 % yield of hydrogenation products). An alternative mechanism for production of the propylene glycol propyl ether is ionic hydrogenation of the 2-ethyl-4-methyl-1,3-dioxolane, shown for one isomer in Equation (4). This acetal



(4)

was independently synthesized and converted to *n*-propanol and propylene glycol propyl ether under the same catalytic reaction conditions. Similarly, a plausible route for production of the di-*n*-propyl ether would involve formation of a hemiacetal from the reaction of *n*-propanol with propionaldehyde, followed by deoxygenation of the hemiacetal to generate di-*n*-propyl ether.

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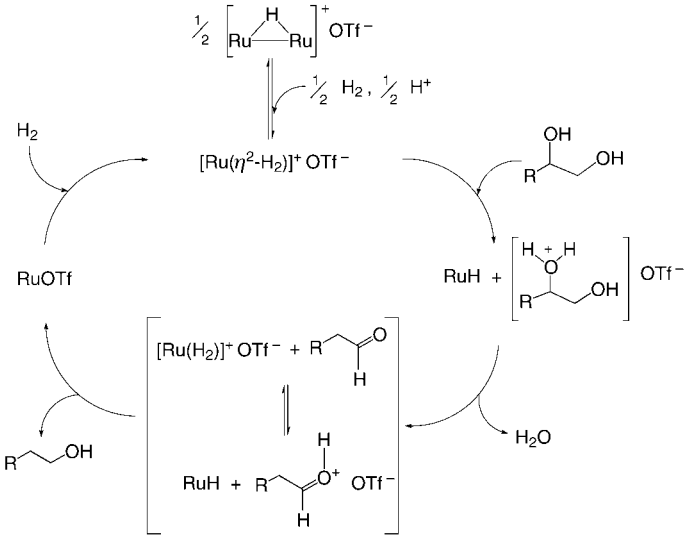
Because of the formation of the condensation products and the associated equilibria, the kinetic profile of the reaction is complicated, and a detailed kinetic analysis has not been attempted. A key problem is the determination of the actual water concentration in the reaction mixture at any given time, and its influence on the position of the condensation equilibria and catalyst performance.

Most experiments were conveniently carried out with a starting pressure of 5.2 MPa (750 psi), but only small changes in the rate of catalysis were observed over the pressure range of 0.7 – 28 MPa. Indeed, catalytic deoxygenation was even achieved by bubbling H_2 at atmospheric pressure through the solution.

The proposed primary mechanism for the deoxygenation reaction is shown in Scheme 1. Cleavage of the two hydride-bridged ruthenium atoms by H_2, in the presence of HOTf,

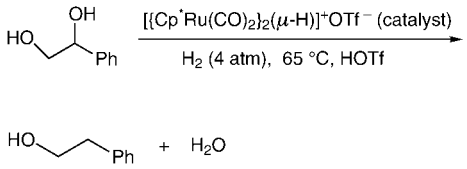


Scheme 1. Proposed mechanism for catalytic deoxygenation.

would produce the dihydrogen complex $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$. Heinekey and co-workers have previously shown[11] that $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$ can be prepared by protonation of $[Cp^*Ru(CO)_2H]$, but that it decomposes below room temperature to give $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+$, H_2, and H^+.

The mechanism proposed in Scheme 1 shows the reverse of their reaction, which regenerates $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$. Further evidence for this equilibrium comes from our observation by ^2H NMR spectroscopy of $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}D)]^+$ from the reaction of $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+$ with D_2 at 100 °C. Acid-catalyzed dehydration of propanediol generates propionaldehyde, which is observed under our reaction conditions. This dehydration may be catalyzed by free HOTf rather than by the ruthenium complex only, but the route shown appears feasible, in view of the remarkable acidity found[11] for $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$. The C=O bond of the propionaldehyde would then be hydrogenated in an ionic hydrogenation mechanism[2] involving protonation of the aldehyde by $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$, followed by hydride transfer to the protonated aldehyde by $[Cp^*Ru(CO)_2H]$. Release of the alcohol product generates $[Cp^*Ru(CO)_2OT_f]$, which then reacts with H_2 to regenerate $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$ and complete the catalytic cycle. Employing $[Cp^*Ru(CO)_2OT_f]$ as the catalyst precursor gave essentially the same reactivity as that found with $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+$, consistent with the proposed mechanism. Further mechanistic studies are underway.

Our studies to date have focused on the deoxygenation of 1,2-propanediol, but a similar catalytic deoxygenation of 1-phenyl-1,2-ethanediol to 2-phenylethanol [Eq. (5)] was also



(5)

found. This reaction proceeds under milder conditions (65 °C) but has only been studied thus far in NMR tubes in CD_2Cl_2, precluding a quantitative comparision to the deoxygenation of 1,2-propanediol. Preliminary results show that glycerol can also be deoxygenated, but the reaction has not yet been optimized, and further studies are needed. Reaction of glycerol (1.0 M) with $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+OTf^-$ (10 mM) and 60 mM HOTf under H_2 (5.2 MPa) at 110 °C in sulfolane for 19 h gave 1,3-propanediol (2.9 turnovers based on $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+$), 1,2-propanediol (0.9 turnovers), and *n*-propanol (3.1 turnovers). A similar experiment with higher HOTf (120 mM) produced no detectable (< 0.3 turnovers) 1,2-propanediol, with larger amounts of 1,3-propanediol (4.6 turnovers) and *n*-propanol (5.7 turnovers). Product mixtures were also reported from prior attempts to develop homogeneous catalysts for deoxygenation of glycerol.[12] These latter reactions were carried out under CO/H_2 mixtures, and higher temperatures and often higher pressures were employed than those in our work.

These results provide a highly selective catalytic method for deoxygenation of diols, a reaction that normally requires more than one step to accomplish in a stoichiometric transformation. This new approach may ultimately lead to a process that has utility for biomass conversions.

Experimental Section

In a drybox, a sulfolane solution (40 mL) containing 1,2-propanediol (1.0 M), $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+OTf^-$ (0.147 g, 0.200 mmol, 5 mM), and toluene (0.1 M, internal standard for integration) was placed in a Parr autoclave, and CF_3SO_3H (213 μL, 2.40 mmol, 60 mM) was added dropwise. The autoclave was sealed, and the solution was heated to 110 °C under H_2 (5.2 MPa initial pressure before heating). The progress of the reaction was quantitatively monitored by gas chromatography. After 30 h, 0.08 M (8 %) of the 1,2-propanediol remained, and the concentrations and yields of hydrogenated products were *n*-propanol (0.54 M, 54 %), propylene glycol propyl ether (0.11 M, 11 %), and di-*n*-propyl ether (0.074 M, 15 %), for a total yield of hydrogenation equivalents of 80 % yield. The di-*n*-propyl ether is considered as two hydrogenation equivalents, since two equivalents of *n*-propanol are required to produce one equivalent of di-*n*-propyl ether. The mass balance of identified products was generally 90 – 100 % in this and related reations.

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[1] P. A. Chaloner, M. A. Esteruelas, F. Joó, L. A. Oro, *Homogeneous Hydrogenation*, Kluwer Academic, Boston, **1994**.
[2] R. M. Bullock, M. H. Voges, *J. Am. Chem. Soc.* **2000**, *122*, 12594 – 12595.
[3] M. P. Magee, J. R. Norton, *J. Am. Chem. Soc.* **2001**, *123*, 1778 – 1779.
[4] a) Y. Blum, D. Czarkie, Y. Rahamim, Y. Shvo, *Organometallics* **1985**, *4*, 1459 – 1461; b) Y. Shvo, D. Czarkie, Y. Rahamim, D. F. Chodosh, *J. Am. Chem. Soc.* **1986**, *108*, 7400.
[5] C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana, *J. Am. Chem. Soc.* **2001**, *123*, 1090 – 1100.
[6] a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97 – 102; b) M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466 – 1478.
[7] For reviews, see: S. W. McCombie in *Comprehensive Organic Synthesis*, *Vol. 8* (Ed.: B. M. Trost), Pergamon Press, New York, **1991**, chap. 4.2; b) W. Hartwig, *Tetrahedron* **1983**, *39*, 2609 – 2645.
[8] For example, the classical Barton – McCombie reaction entails conversion of an alcohol to a thiocarbonyl derivative, which is then reduced to the deoxygenated product by using nBu$_3$SnH: D. H. R. Barton, S. W. McCombie, *J. Chem. Soc. Perkin Trans. 1* **1975**, 1574 – 1585. A modification was developed in which the Sn reagent is used in catalytic amounts, but it still uses stoichiometric amounts of a main group hydride (SiH): R. M. Lopez, D. S. Hays, G. C. Fu, *J. Am. Chem. Soc.* **1997**, *119*, 6949 – 6950.
[9] F. W. Lichtenthaler, S. Mondel, *Pure Appl. Chem.* **1997**, *69*, 1853 – 1866.
[10] A. Stasunik, W. Malisch, *J. Organomet. Chem.* **1984**, *270*, C56 – C62.
[11] M. S. Chinn, D. M. Heinekey, N. G. Payne, C. D. Sofield, *Organometallics* **1989**, *8*, 1824 – 1826.
[12] G. Braca, A. M. Raspolli Galletti, G. Sbrana, *J. Organomet. Chem.* **1991**, *417*, 41 – 49; b) E. Drent, W. W. Jager, US Patent 6080898, **2000**, [*Chem. Abstr.* **1999**, *130*, 126585r]; c) T. M. Che, US Patent 4642394, **1987**, [Chem. Abstr. **1987**, *106*, 121849z].

Probing Transient Hydrate Structures with Hyperpolarized ^{129}Xe NMR Spectroscopy: A Metastable Structure II Hydrate of Xe

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The formation of gas hydrates involves the reaction of water or ice with small hydrophobic atoms or molecules in the size range of about 4.0 (Ar) to about 8.0 Å (methylcyclohexane).[1] Several hydrate structural families are known, and these are designated as structure I, II, and H (Str. I, Str. II and Str. H), the structure usually being determined by the largest guest in the hydrate.[1] Many questions remain about the nucleation of hydrates, their growth, and inhibition.[2] Such issues are of importance in a number of areas, as hydrates exist both in nature and in industrial environments.[2] To learn to control hydrate formation and decomposition is of continuing interest, especially to solve hydrate control problems in the hydrocarbon resource industry.[2]

Methods capable of monitoring hydrate formation processes are relatively few, especially if molecular-scale information is desired. Vibrational and NMR spectroscopies do have such capabilities.[3, 4] For the latter, the chemical shift tensors or isotropic shifts of molecules in different guest sites can be observed, and in this way provide a signature that is characteristic of the structural type.[4] ^{129}Xe was the first guest to be used this way;[5] however, as the time required to record Xe NMR spectra is significant because of long spin-lattice relaxation times, it is not a suitable probe for studying processes. Advances in the development of optical pumping techniques for producing highly polarized Xe (HP Xe)[6] have solved this problem, and it has already been demonstrated that kinetic studies of hydrate formation can be carried out on a subsecond time scale.[7, 8] Herein we draw attention to the HP Xe approach as a powerful way of observing transient behavior and thereby yielding structural information in a time-resolved fashion. We show that unusual phenomena observed when HP Xe is placed in contact with a Str. II hydrate of tetrahydrofuran give new insights into hydrate formation reactions at the molecular level.

The experiment in which we were interested involved the exposure of a Str. II hydrate with empty small cages to a Str. I guest. In the case of THF hydrate, THF occupies the large cages in Str. II hydrate which has a crystal structure with a unit cell that can be formulated as $16\,M_s \cdot 8\,M_l \cdot 136\,H_2O$, where M_s and M_l are the small (5^{12}) and large cages ($5^{12}6^4$), respectively (where 5^{12} corresponds to a cage with twelve five-sided faces). In Str. II hydrate the small cages may be empty or they may be occupied by small molecules such as Ar, Kr, Xe, N_2, O_2, and CH_4. On the other hand, Xe on its own forms a Str. I hydrate, with a structural designation of $2\,M_s \cdot 6\,M_l \cdot 46\,H_20$, where M_s is a 5^{12} cage and M_l is the $5^{12}6^2$cage.

Experiments were carried out on a Bruker AMX-300 NMR spectrometer (magnetic field 7.05 T, ^{129}Xe resonance frequency 83.03 MHz) by exposing powdered Str. II THF hydrate samples to HP Xe gas, which was prepared by optical pumping[6] directly in the NMR probe.[9, 10]

The time development of the Xe spectrum is shown in Figure 1. For closer scrutiny, selected spectra, along with those obtained for a control sample of powdered ice, are shown in

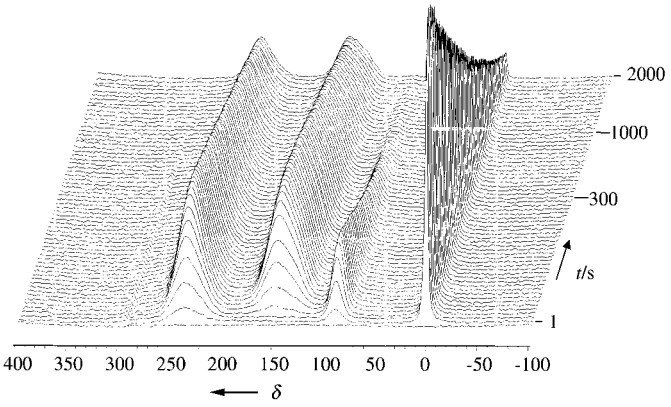

Figure 1. Time development of the ^{129}Xe NMR spectrum after exposure of a powdered THF sample to hyperpolarized Xe. The line at $\delta \approx 0$ can be assigned to the gas, the lines at $\delta \approx 90$, 150, and 240 to Xe in the large cage of Str. II, the large cage of Str. I, and the two small cages in the Str. I and Str. II, respectively. Experimental conditions: temperature 223 K; starting pressure of Xe 530 mbar. Before adsorption of HP xenon, the sample was evacuated for 30 – 40 min at 10^{-5} mbar to minimize the presence of adsorbed oxygen.

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