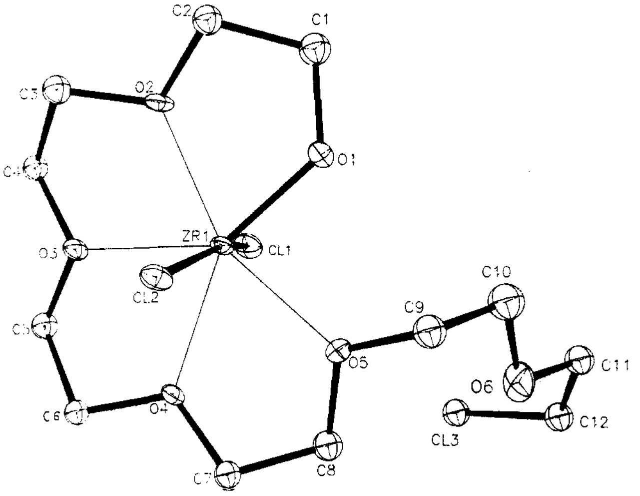


Figure 1. View of the $[ZrCl_2{\cdot}(OCH_2CH_2)_5OCH_2CH_2Cl]^+$ cation.

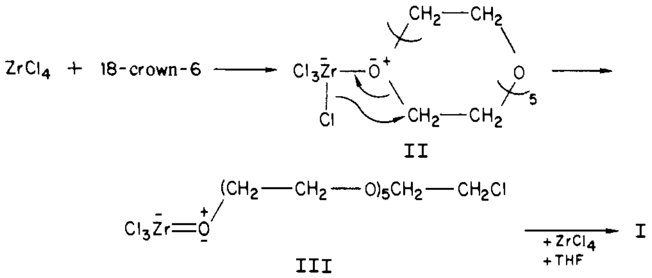
$H_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$ (I).[4]

The structure of the novel cation is shown in Figure 1. The zirconium atom is seven-coordinate, with the macrocycle filling the five equatorial sites. The Zr–O(1) interaction is a full covalent bond at 1.93 (2) Å.[5,6] The remainng Zr–O lengths range from 2.24 to 2.33 Å and are typical for donor–acceptor bonds.[7] The five zirconium-bonded oxygen atoms are planar to within 0.08 Å, and the Zr atom lies 0.03 Å out of the plane.

The macrocycle appears to be quite similar to 15-crown-5 in its ability to coordinate the metal.[8] The O···O separations, 2.49 to 2.65 Å, are close to those found in complexes of the crown ether with the exception of O(1)···O(5) at 2.72 Å. O(6) is not needed to fill out the coordination sphere of the zirconium, and it does not interact with the metal. The terminal chlorine atom exhibits high thermal motion, but the Cl–C bond length of 1.71 Å is near the ideal value (the high esd notwithstanding).

The transfer of halide from an early transition metal to a hydrocarbon has precedent in the pyrolysis of the diethyl ether complexes of $NbCl_5$ and $TaCl_5$ to give ethyl chloride and metal oxy trihalides.[9] This information, combined with the known propensity of $ZrCl_4$ to break C–O bonds in donor complexes because of the strength of the Zr–O bond,[10] has led us to propose the reaction pathway shown in Scheme I. First, an oxygen atom of the crown ether adds in a donor fashion to the zirconium atom forming II. In the second step one can envision the transfer of a chlorine atom to the α-carbon with breakage of the C–O bond to give III. In the third step a chloride ion is abstracted from the zirconium atom containing a partial negative charge by a $ZrCl_4$ unit in the presence of THF. Note that this is offered only as a reasonable possibility.

Scheme I



The anion is an interesting species. The $[ZrCl_6]^{2-}$ ion is well-known, but the only reference to a $ZrCl_5^-$ species is an infrared spectrum attributed to $[PCl_4][ZrCl_5]$.[11] However, the corresponding titanium-continuing anion was recently reported.[12] The geometry about the zirconium atom is a nearly perfect octahedron. The Zr–Cl lengths range from 2.388 (8) to 2.452 (7) Å. These values compare favorably with both the literature values and with the 2.434 (8) Å distance found in the cation.

Acknowledgment. We are grateful to the National Science Foundation and to the Department of Energy for support of this research. Thanks are also offered to Dr. U. Kynast for recording and interpreting the IR data.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, observed and calculated structure factors, and IR absorptions with tentative assignments (17 pages). Ordering information is given on any current masthead page.

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(4) A solution of18-crown-6 (1.59 g, 6 mmol) in toluene was added to a suspension of $ZrCl_4$ (1.40 g, 6 mmol) in toluene. THF was added up to 15% by volume, and the tube was sealed and heated to 100 °C for 24 h. Upon cooling to room temperature, colorless, air-sensitive crystals formed in ca. 25% yield. The crystals belong to the triclinic space group $P\bar{1}$; cell constants, $a = 7.238$ (7) Å, $b = 13.754$ (6) Å, $c = 16.378$ (9) Å, $\alpha = 105.52$ (4)°, $\beta = 91.17$ (4)°, $\gamma = 98.17$ (4)° with two formula units per unit cell and $D_c = 1.72$ g cm^{-3}. Least-squares refinement based on 1751 observed reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.068$. The details of data collection and refinement are as given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. An empirical absorption correction was done according to Churchill and Hollander: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957. Anisotropic thermal parameters were used for Zr, Cl, and O atoms. Hydrogen atoms were not located.

(5) Atwood, J. L.; Rogers, R. D.; Bynum, R. V. *Acta Crystallogr., Sect. C* **1984**, *C40*, 1812 and references therein.

(6) The Zr–O stretch in the IR corresponding to the covalent linkage appears as a very strong band at 750 cm^{-1}. A complete listing of IR absorptions may be found in the supplementary material.

(7) The Zr–O lengths are 2.24 (1), 2.25 (1), 2.33 (1), and 2.24 (1) Å for O(2) to O(5), respectively. They may be compared with the Zr–O distance in the anion of 2.24 (2) Å.

(8) Although there is no related complex between 15-crown-5 and $ZrCl_2^{2+}$, comparisons can be made with regard to 15-crown-5·$AlCl_2^+$ (ref 1) and 15-crown-5·$YbCl_2^+$ (Atwood, D. A.; Bott, S. G.; Atwood, J. L., unpublished results).

(9) Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* **1958**, 3133.

(10) Early transition metal halides are known to cleave a C–O bond in THF. For a recent account, see: Bartmann, E. *J. Organomet. Chem.* **1985**, *284*, 149.

(11) Demiray, A. F.; Brockner, W. *Monatsh. Chem.* **1980**, *111*, 21.

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(13) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

Thermally Activated Magnesium Oxide as a Selective Deuteration Catalyst under Mild Conditions

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Alkaline-earth oxides are readily available materials that possess remarkable chemical properties when thermally activated. Basic sites (H^+ abstraction sites),[1] reducing sites[2,3] (electron-transfer sites), and radical sites (H· abstraction sites)[4] have all been utilized on the surface of high surface area polycrystalline MgO.

Due to this wealth of interesting chemistry and the abundance of MgO and CaO, we have initiated a program involving the use of these materials as catalysts and/or stoichiometric reagents for carrying out organic/inorganic syntheses.[5] In this paper we report on MgO as a catalyst for carrying out selective hydrocarbon–D_2 exchange.

Hydrogen–deuterium exchange reactions over metal oxide catalysts have been observed before. Hall and co-workers[6] and

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(1) Utiyama, M.; Hattori, H.; Tanabe, K. *J. Catal.* **1978**, *53*, 237–242.

(2) Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970.

(3) Morris, R. M.; Klabunde, K. J. *Inorg. Chem.* **1983**, *22*, 682–687.

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(6) Larson, J. G.; Hall, W. K. *J. Phys. Chem.* **1965**, *69*, 3080–3089.

Burwell and co-workers[7] have shown that Al_2O_3 and Cr_2O_3 exhibit unusual activities for such processes. Likewise, Flockhart and co-workers[8] have studied the propene–D_2 system and have correlated activity with oxidizing sites on the Al_2O_3. However, Robertson and co-workers[9] have demonstrated that activity is a function of the acidity of the hydrocarbon. Similarly, Utiyama, Hattori, and Tanabe[1] have shown that several basic oxides (MgO, CaO, SrO, BaO, and La_2O_3) are active in the CH_4–D_2 exchange reaction and also believe carbanions are intermediates.

The H_2–$D_2 \rightarrow$ HD exchange over activated MgO has also been studied in detail.[10] Extremely low activation energies for this process, about 2 kcal/mol, were reported.

Although the exact nature of the active sites for these processes is controversial, it appears that completely heterolytic processes are involved ($R\text{–}H \rightarrow R^-_{ads} + H^+_{ads}$) as opposed to metallic based catalysts ($R\text{–}H \rightarrow R\cdot_{ads} + H\cdot_{ads}$). This heterolytic carbanion formation process was given additional strong support by Garrone and Stone[11] who measured relative amounts of carbanions formed by allowing them to react with O_2 and measuring the amount of O_2^- formed by ESR. Analysis of a series of carbon acids suggested that their reactivities on MgO paralleled their solution-phase acidities. This study coupled with the earlier reports mentioned encouraged the present study.

Selective Deuteration. Magnesium oxide (99.999%) was boiled with distilled water for 1 h, recovered by hot filtration, dried in air at 110 °C for 10 h, and chopped into small pieces (~2 mm). About 100 mg of this hydrated oxide (9–12 pieces) was placed in a recirculation flow reactor,[12] constructed so that the MgO could be activated by evacuation ($\sim 3 \times 10^{-3}$ torr) at 660 °C for 6 h. After cooling, purified[13] hydrocarbon/D_2 mixtures could be continuously flowed over the activated MgO at any desired temperature. When a gaseous mixture of toluene (6 torr)/D_2 (110 torr) was allowed to recirculate over 0.075 g of MgO at 25 °C, complete exchange of the methyl group hydrogen ($CH_3 \rightarrow CD_3$) occurred within 0.5 h. According to MS and NMR results, no appreciable amount of deuterium was incorporated into the phenyl ring under these conditions. However, upon exposure to the catalyst at 300 °C, complete phenyl ring deuteration could be achieved. Similar results were obtained with xylenes: that is, CH_3 deuteration first and, under more strenuous conditions, phenyl ring deuteration. And, as might be expected, benzene was cleanly deuterated under conditions where phenyl ring deuteration of toluene or xylene occurred. These data indicate that acidity of the C–H bond is important, thus the more facile deuteration of benzylic C–H sites compared with aromatic C–H sites.

Ethylbenzene provides the most striking example. In this case the benzylic hydrogens were exchanged completely at 25 °C, as clearly shown by NMR. Deuteration at higher temperature caused first ring deuteration followed by deuteration of the CH_3 group (which of course is non-benzylic). These results also support the concept that acidity of the C–H bond is the determining factor since the known acidity order is benzylic CH > aromatic CH > aliphatic CH.[14]

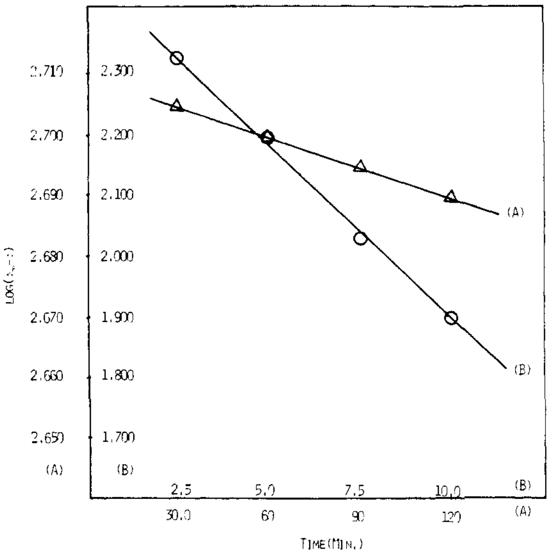

Figure 1. Kinetic plots of deuteration for benzene and toluene with D_2 over activated MgO: (A) and outer scale for deuteration of benzene at 100 °C and (B) and inner scale for methyl deuteration of toluene at 50 °C.

Table I. Kinetic Data for X–H/D_2 Exchange Reactions

X–H	catalyst[a,b]	temp/°C	k_ϕ/unit[c]	turnover frequency ($\times 10^3$)[d]	E_a/(kcal/mol^{-1})
toluene		25	7.2[e]	53.4	0.9
	1	50	8.2	60.8	
	2	50	8.3	61.6	
	3	100	10.3	76.4	
	4	150	11.7	86.8	
	5	200	13.2	98.0	
		300	16.2	120.0	
benzene		25	0.0028[e]	0.0207	8.1
	6	100	0.044	0.326	
	7	150	0.21	1.56	
	8	200	0.42	3.12	
	9	250	1.0	7.42	
	10	300	1.9	14.1	

[a] 0.075 g of MgO obtained by evacuating 0.10 g of Mg/$\cdot x H_2O$ at 660 °C for 6 h. Each catalyst is a different MgO sample. [b] Repeated experiments with different catalyst samples showed good reproducibility (<±4%). For example, see catalyst samples 1 and 2. [c] Unit = no. of D atoms entering 100 X–H molecules per second per gram of MgO. [d] No. of D entering all molecules per nanometer squared of MgO per second (based on a surface area of MgO of 130 m^2/g. [e] Calculated from graphical extrapolation of $1/T$ vs. log k_ϕ plots.

Kinetic Studies. The remarkable selectivity allowed by this heterogeneous catalyst prompted us to carry out kinetic analyses. Toluene (CH_3 group) serves as the model for benzylic hydrogen exchange, which is apparently a low activation energy process, and benzene serves as the model for aromatic hydrogen exchange.

$$X\text{–}H(6\text{ torr}) + D_2(110\text{ torr}) \xrightarrow{MgO} X\text{–}D + HD$$

$$X = C_6H_5CH_2,\ C_6H_5$$

These reactions were well behaved in the 25–300 °C range, and first-order rate constants, k_ϕ, were calculated from plots of log ($\phi_\infty - \phi$) vs time, using the equation[1,15]

$$\log(\phi_\infty - \phi) = -\frac{k_\phi W t}{2.303\phi_\infty} + \text{constant}$$

where ϕ is the mean deuterium content at any stage of the reaction at time t, ϕ_∞ is the value at equilibrium, and W is the weight of the catalyst. Figure 1 and Table I summarize the data indicating

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(7) (a) Burwell, R. L., Jr.; Littlewood, A. B.; Cardew, M.; Pass, G.; Stoddard, C. T. H. *J. Am. Chem. Soc.* **1960**, *82*, 6272–6280. (b) Burwell, R. L.; Haller, G. L.; Taylor, K. C.; Read, J. F. *Adv. Catal.* **1969**, *20*, 1.

(8) Flockhart, B. D.; Uppal, S. S.; Pink, R. C. *Trans. Faraday Soc.* **1971**, *67*, 513–525.

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(10) Boudart, M.; Delbouille, A.; Derouane, E. G.; Indovina, V.; Walters, A. B. *J. Am. Chem. Soc.* **1972**, *94*, 6622–6630.

(11) Garrone, E.; Stone, F. S. *Proc. Int. Congr. Catal., 8th* **1984**, *3*, 441–452.

(12) Tanaka, Y.; Klabunde, K. J. *J. Mol. Catal.* **1983**, *21*, 57–79. A detailed description will be included in the full paper describing the present work.

(13) Deuterium (99.5%, Matheson) was purified and stored as described previously. Before use, toluene (certified A.C.S. Fischer Scientific) and benzene (reagent A.C.S., MCB) were stored over CaH_2 more than 1 week, then passed as a vapor through 4-Å molecular sieves (10 °C) and then activated MgO (10 °C), and then stored over 4-Å molecular sieves (all sieves were activated at 300 °C under vacuum before use).

(14) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; p 19.

(15) Kemball, C. *Adv. Catal.* **1959**, *11*, 226–230.

good reproducibility for experiments with different catalysts samples.

Activation energies E_a were obtained from plots of $1/T$ vs. log k_ϕ. For benzylic hydrogen exchange, $E_a = 0.9$ kcal/mol, and for aromatic hydrogen exchange, $E_a = 8$ kcal/mol.[16-18] These results clearly explain why such selective benzylic deuteration is possible. As would be expected, the ratios k_ϕ(toluene)/k_ϕ(benzene) increase dramatically as temperature is lowered. For example at 25 °C this ratio is 2570, at 100 °C, 234, at 200 °C, 31, and at 300 °C it is 8.5 (see Table I). Also, such a low E_a for benzylic exchange predicts that exchange could occur at very low temperature; indeed we have observed such exchange at below −100 °C, and these results will be reported fully later.

Acknowledgment. The support of the Army Research Office under Grant DAAG29-84-K-0051 is appreciated.

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(16) We believe these E_a values are correct and not influenced by restricted internal diffusion of the hydrocarbons through the MgO particles. First of all, the particles are extremely porous, crumbling to a fine powder upon being touched lightly. Furthermore, these MgO samples have large surface areas (130-170 m^2/g) and large pore diameters (25-75 Å).[3]

(17) Note that a high excess of D_2 was employed to minimize complications due to approach to isotopic equilibrium. Although conversions were often carried to >50% good straight line plots of log ($\phi_\infty - \phi$) vs. time were always obtained.

(18) Although only small amounts of toluene were converted while collecting these kinetic data, deuteration of large amounts was possible by continued operation. In other words, the MgO definitely behaves as a catalyst and, as an example, in one large-scale, long-term experiment >50 turnovers took place. We have also used the same catalyst sample over and over again on occasion. We have not yet determined the maximum number of turnovers possible.

Serial Radical Cyclization via a Vinyl Group Immobilized by a Pyranoside. A Route to Bis-Annulated Pyranosides[1]

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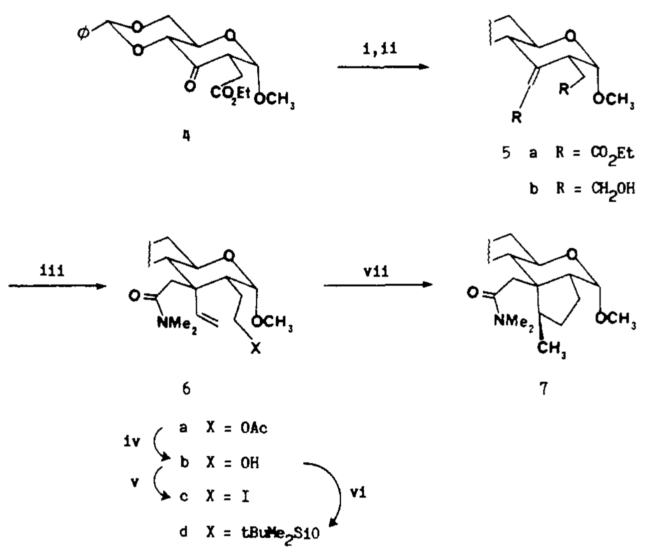
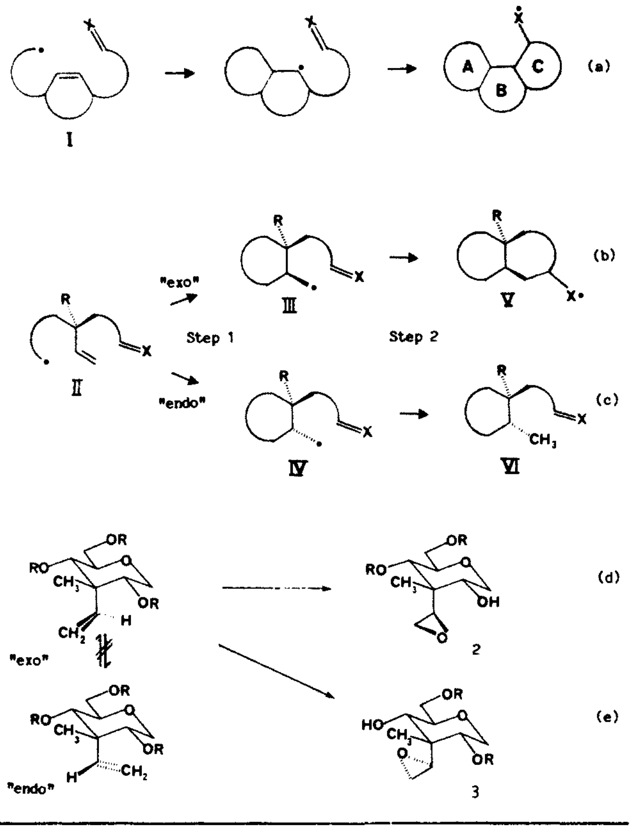
Received November 7, 1985

Three vibrant areas of chemical research are currently (i) the synthetic potential of free radical reactions,[2-7] (ii) the synthesis of polyquinanes,[8-10] and (iii) the utility of carbohydrates in organic synthesis.[11-14] The combination of (i) and (ii) has been cleverly explored by Curran[8] and Beckwith[9] in the context of the linearly fused triquinanes, and a combination of (i) and (iii) has received evaluation by Giese,[4] Vasella,[14] and Wilcox.[15] The surprising suitability of carbohydrates as substrates for free radical reactions had been noted previously in this laboratory in connection with photochemical induced alkylation reactions.[16,17] In this paper we describe a novel combination of (i)-(iii), which has implications

Scheme I[a]



[a] (i) Ph_3PCHCO_2Et (86%); (ii) DIBALH (76%); (iii) $CH_3C(OMe)_2NMe_2$ (98%); (ii) NaOMe/MeOH (100%); (v) Ph_3P, I_2 (94%); (vi) t-$BuMe_2SiCl$ (100%); (vii) (n-$Bu)_3SnH$ (98%).



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