

Table I. Oxidation of Cyclododecanol by Permanganate-Coated Supports

Re-agent	Support	Loading, ^a mmol of KMnO ₄ / g of reagent	Oxidizing capacity, ^b mmol of alcohol/ g of reagent	t _{1/2} , h ^c
1	LMS ^d 3A (1/16-in. pellets)	0.17	0.08	19.0
2	LMS 4A (1/16-in. pellets)	0.22	0.22	1.0
3	LMS 5A (1/16-in. pellets)	0.25	0.10	2.0
4	LMS 13X (1/16-in. pellets)	0.27	0.23	0.5
5	LMS 4A (4-8 mesh)	0.09	0.04	70.0
6	LMS 4A (8-12 mesh)	0.23	0.12	9.0
7	LMS 13X (powder)		0.56	
8	Silica gel (100-200 mesh)		0.30	
9	K-10 Montmorillonite clay (powder)		0.40	
10	K-306 Montmorillonite clay (powder)		0.34	
11	K-306 Montmorillonite clay (spheres)		0.06	

^a Determined by UV analysis. ^b Determined by reaction of 0.5 g of the reagent with an excess of cyclododecanol (0.5 mmol) in 3 mL of benzene at 70 °C for 72 h. ^c The time required for one-half conversion of cyclododecanol to cyclododecanone is tabulated as an approximate indication of the relative rates of reaction; values listed refer to the oxidation of 0.05 mmol of cyclododecanol in 3 mL of benzene at 70 °C with a mole ratio of sieve-bound KMnO₄ to alcohol of 6:1. ^d Linde Molecular Sieve (LMS)

Table II. Oxidation of Alcohols by Permanganate Coated Molecular Sieves^a

Alcohol	Product	Time, h	Yield, % ^b
Benzhydrol	Benzophenone	7	100
2-Octanol	2-Octanone	7	92 (82) ^c
Cycloheptanol	Cycloheptanone	7	94
Cyclooctanol	Cyclooctanone	7	90 (87) ^c
Cyclododecanol	Cyclododecanone	7	95 (90) ^c
1-Octanol	Octanal	4	26
Benzyl alcohol ^d	Benzaldehyde	2	80
Cinnamyl alcohol	Cinnamaldehyde	2	93 (94) ^c
1-Hexanol	Hexanal	6	29
1-Decanol	Decanal	9	26
1-Dodecanol	Lauraldehyde	6	34
3β-Cholestanol	3-Cholestanone	4	(91) ^c

^a Unless noted otherwise, oxidation of 0.1 mmol of the indicated alcohol was carried out in 3 mL of benzene at 70 °C using potassium permanganate-coated Linde 4A (1/16-in. pellets) Molecular Sieves (1.5 g). ^b Yields were determined by GLC using internal standards. ^c Isolated yield from preparative-scale reaction using procedures similar that described for the oxidation of cyclododecanol. ^d The amount of sieve/KMnO₄ reagent used was 1.0 g.

petitive with the most convenient of existing methods for small-scale oxidations of secondary alcohols to ketones.¹³

Data which will be presented in subsequent papers indicate that potassium permanganate is not unique in its ability to become activated through impregnation onto molecular sieves. We have found, for example, that sodium cyanide impregnated on Linde 13X Molecular Sieves reacts at 110 °C with 1-bromooctane dissolved in benzene to give high yields of 1-cyano-octane.¹⁴ Attempted reaction of sodium cyanide pellets or aqueous sodium cyanide solution with 1-bromooctane in benzene under similar conditions gave no detectable 1-cyano-octane. Although we do not have as yet a clear under-

standing of the principal factor (or factors) responsible for the rate enhancement observed in these systems, taken together, these results do suggest that activation of reagents through impregnation onto inorganic supports may provide an attractive synthetic alternative to related techniques such as phase transfer¹⁵ and triphase catalysis.^{16,17}

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References and Notes

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- (3) D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **94**, 4024 (1972).
- (4) Commercial sieves in pelleted form contain 20% clay binder in addition to the parent zeolite. We are grateful to Dr. Marvin Poutsma for bringing this to our attention.
- (5) Linde Molecular Sieves were purchased from Alpha Chemicals, Danvers, Mass., and used as obtained.
- (6) The bath temperature was kept below 65 °C.
- (7) Potassium permanganate was removed from a weighed portion of sieve/KMnO₄ for quantitative analysis (UV) by extensive washing with distilled water. The procedures used for both the preparation and analysis of the reagent have been employed several times giving reproducible results. The loading of 0.27 mmol of KMnO₄/g of reagent appears to be the maximum obtainable for this system.
- (8) An authentic sample from Aldrich Chemical Co. had mp 57-61 °C.
- (9) Fisher reagent grade potassium permanganate was pulverized in a mortar prior to addition.
- (10) Procedures used for the preparation of each of the reagents listed in Table I were similar to that described for impregnation of KMnO₄ onto Linde 13X (1/16-in. pellets), except for reagents 7-11, where nonadsorbed permanganate was not removed.
- (11) The stoichiometry of these oxidations has not been established. Whether a portion of the adsorbed permanganate is unreactive or whether 1 mol of permanganate oxidizes <1.5 mmol of alcohol (stoichiometry expected if permanganate goes to MnO₂) is not presently clear.
- (12) Aldehydes formed in these reactions undergo further oxidation to the corresponding carboxylic acid.
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- (17) For other recent reports of reagents impregnated on inorganic supports, see E. C. Taylor, C. S. Chiang, A. McKillip, and J. F. White, *J. Am. Chem. Soc.*, **98**, 6750 (1976), and references cited therein.

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Microenvironment within a Solid-Phase Cosolvent¹

Sir:

We have recently shown that a graft copolymer derived from poly(ethylene glycol monomethyl ether) and cross-linked polystyrene exhibits triphase catalytic activity for certain hydrolysis and displacement reactions.^{2,3} It was suggested that the insoluble polymer acts as a cosolvent. Before a detailed understanding of these catalytic processes is possible, the microenvironment within the resin must be defined. In an attempt to acquire pertinent information, we have applied the spin-probe technique to this problem and now wish to report prin-

to be a rigid matrix, decreasing the size of the solvent channel "squeezes" the nitroxide from the channel interior onto the polymer-water interface where it feels the influence of the rigid nonpolar resin. If the polymer is considered mobile, decreasing the water content decreases the mole fraction of water and increases the internal viscosity. Based upon EPR and chemical studies, it is now clear that, for solvent-swelled cross-linked polystyrene, both pendant groups and the polymer backbone have significant mobility.^{9,10} Resin **1** appears to have similar properties and we, therefore, prefer to adopt the cosolvent model.¹¹

Although we expected little difference between a_N for **2** imbibed as a toluene solution in **1**, with that measured for **2** in pure toluene or 1,2-dimethoxyethane, we have observed a slightly higher value under conditions of low swelling (entry 4). This difference may result in part from trace amounts of tenaciously bound water in **1**. Comparison of entry 4 with 7 strongly suggests that imbibed water can contribute to the polarity of the environment experienced by **2**. Control experiments carried out in which unfunctionalized polystyrene was swelled with limited amounts of water-saturated toluene containing **2** indicate a large degree of immobilization of the probe but no significant change in the polarity of its environment (entries 2 and 5).

Triphase Conditions. When **1** was swelled with an excess of both water and toluene and the external liquid phases removed by rapid suction filtration, the polarity within the polymer as revealed by **2** was equivalent to that of $X_{H_2O} = 0.25$ for water-1,2-dimethoxyethane (entry 6). In contrast, **3** indicated that, for a similarly swelled resin, the internal polarity is comparable to $X_{H_2O} = 0.97$ (entry 14). These data clearly establish the existence of relatively fluid polar and nonpolar zones within the polymer. Additional support for this conclusion comes from the EPR spectrum of 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy imbibed in **1** under similar triphase conditions. Here, spectral distortion not found in **2** and **3** is readily apparent (most notably, the high field peak is replaced by two lines). This distortion is undoubtedly derived from the nitroxide located in two regions of significantly different polarity; in addition, exchange between the zones must be slow relative to the EPR time scale.^{12,13} With the water content constant, decreasing the amount of toluene results in a steady increase in a_N and W values for **2** (entries 6-8). Although time averaging of signals of **2** partitioned between polar and nonpolar zones accounts for this trend, the very large increase in W clearly indicates that the spin probe is not relocating completely into the fluid interior of the polar zone (compare entry 8 with 16).¹⁴ When the toluene content is constant and the amount of water is reduced, a_N decreases and W increases for nitroxide **3** (entries 14 and 15). These data are consistent with (a) contraction of the nonpolar (polar) zone "squeezing" **2** (**3**) onto a polar-nonpolar interface¹⁵ and/or (b) the polarity and viscosity of the interior of the polar and nonpolar zones being variable. At present we cannot assess the importance of each of these possibilities.

Experiments now in progress are aimed at correlating EPR measurements of the type described here with catalytic activity of a series of related resins for both displacement and hydrolysis reactions in an effort to gain a better understanding of the nature of the catalysis.

References and Notes

- (1) This work was supported by the National Science Foundation (Grant No. MPS74-23925) and the U.S. Army Research Office (Grant No. DAAG-29-76-G-0330).
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- (11) EPR measurements made of a polymer similar to **1** containing a low concentration of covalently bonded 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl⁹ indicated very rapid tumbling of the spin label under both biphasic and triphase conditions.
- (12) When equilibrated with equal volumes of water and toluene, ~7% of 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy partitioned into the toluene phase.
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- (14) For labels **2** and **3** dissolved in a mixture of water-1,2-dimethoxyethane where $X_{H_2O} = 0.54$, measured W values are 0.06 and 0.10, respectively.
- (15) Menger has proposed a model analogous to that described here for certain spin labels located within water pools of different sizes: F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *J. Am. Chem. Soc.*, **97**, 909 (1975).
- (16) Toluene content was measured by washing the swelled resin with a large volume of ethyl ether and analyzing the filtrate by GLC using an internal standard. Water content was determined by the difference in weight of total imbibed solvent and that of toluene.

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Simple Prediction of Substituent Sensitivity (ρ^+) for Carbocations¹

Sir:

The "tool of increasing electron demand", which has been developed and used extensively by Tanida,^{3a} Gassman,^{3b} and Brown,⁴ has proven to be an important probe of internal participation during solvolyses and of the electron demand of the incipient carbonium ions. The method is generally applied to the solvolyses of a series of tertiary, aryl *p*-nitrobenzoates. By varying the substituents on the aryl ring, the sensitivity of the reaction to the substituents is revealed in the slope (ρ^+) of a Hammett-Brown plot of the logarithm of the rates vs. σ^+ . A very negative ρ^+ indicates the solvolysis is greatly influenced by substituents and that the incipient carbonium ion has high electron demand, e.g., for 7-aryl-7-norbornyl *p*-nitrobenzoates, $\rho^+ = -5.27$.^{3b} Less negative values of ρ^+ are often symptomatic of carbonium ions whose electron demand is diminished by internal charge delocalization, e.g., for *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates, $\rho^+ = -2.30$.^{3b}

We present here a straightforward theoretical method for estimating ρ^+ 's using MO calculations in conjunction with a simple perturbation theory expression. The agreement between theory and experiment establishes that the key factors governing the electron demand of a carbonium ion are the delocalization and energy of the cation's LUMO.

Frontier orbital theory predicts that the important stabilizing interaction for a substituted carbonium ion occurs between the HOMO of the electron donating substituent and the LUMO of the carbonium ion. For an aryl group the appro-