between R_f 0.80–0.90 in the concentrated and dilute runs with enzyme. Although recovery of total counts after scraping was only ca. 25%, starting material and product were well separated on the TLC plate and at least 85% of the radioactivity migrated with pyruvic acid.

References and Notes

(1) We wish to acknowledge the National Institutes of Health (GM 19557), the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

(2) (a) Alfred P. Sloan Fellow, 1975–77; (b) Career Development Award from the National Institutes of Health (HL 00084), 1975–1980.

(3) (a) G. Popjak and J. W. Cornforth, *Biochem. J.*, **101**, 553 (1966); (b) G. Popjak, H. Ngan, and W. Agnew, *Bioorg. Chem.*, **4**, 279 (1975).

(4) D. E. Gregonis and H. C. Rilling, *Biochemistry*, **13**, 1538 (1974).

(5) (a) H. C. Rilling, C. D. Poulter, W. W. Epstein, and B. Larsen, *J. Am. Chem. Soc.*, **93**, 1783 (1971); (b) C. D. Poulter, O. J. Muscio, Jr., and R. J. Goodfellow, *Biochemistry*, **13**, 1530 (1974); (c) C. D. Poulter, *J. Agric. Food Chem.*, **22**, 167 (1974).

(6) C. D. Poulter and J. M. Hughes, *J. Am. Chem. Soc.*, **99**, 3824 (1977).

(7) (a) B. M. Trost, P. Conway, and R. Stanton, *Chem. Commun.*, 1639 (1971); (b) L. Crombie, P. A. Firth, R. P. Houghton, D. A. Whiting, and D. K. Woods, *J. Chem. Soc., Perkin Trans. 1*, 642 (1972); (c) B. M. Trost and W. G. Biddlecom, *J. Org. Chem.*, **38**, 3438 (1973); (d) C. D. Poulter, L. L. Marsh, J.

M. Hughes, J. C. Argyle, D. M. Satterwhite, R. J. Goodfellow, and S. G. Moesinger, *J. Am. Chem. Soc.*, **99**, 3816 (1977).

(8) R. L. Hill and R. A. Bradshaw, *Methods Enzymol.*, **13**, 91 (1969).

(9) (a) R. U. Lemieux and J. Howard, *Can. J. Chem.*, **41**, 308 (1963); (b) C. Donninger and G. Popjak, *Proc. R. Soc., Ser. B*, **163**, 465 (1966).

(10) R. Y. Hsu and H. A. Lardy, *Methods Enzymol.*, **13**, 230 (1969).

(11) This represents a minimum value for the amount of radiolabel retained by the substrate.

(12) In a reduction of deuterated chrysanthemal with yeast alcohol dehydrogenase, we found[6] that the product was slightly enriched in the minor (1S,1'S,3'S) diastereomer. If a similar enrichment occurs with the horse liver enzyme, the corrected R/S ratio would be slightly higher.

(13) (a) C. D. Poulter and C. J. Spillner, *J. Am. Chem. Soc.*, **96**, 7591 (1974); (b) Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971); (c) G. A. Olah, C. L. Jeuell, D. P. Kelley, and R. D. Porter, *ibid.*, **94**, 146 (1972).

(14) (a) H. G. Richie, "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1201; (b) K. B. Wiberg, B. A. Hess, and A. J. Ashe, *ibid.*, p 1295; (c) G. A. Olah, G. Liang, K. A. Babiak, and R. K. Murray, *J. Am. Chem. Soc.*, **96**, 6794 (1974); (d) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303 (1968).

(15) For example, the barrier to rotation about the C(1)–C(1') bond in a primary cyclopropylcarbinyl cation is estimated at 17.5 kcal/mol; L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 6380 (1970).

(16) Y. Kobayashi and D. V. Maudsley, "Biological Applications of Liquid Scintillation Counting", Academic Press, New York, N.Y., 1974, pp 184–189.

(17) C. A. Reece, J. O. Rodin, R. G. Brownlee, W. C. Duncan, and R. M. Silverstein, *Tetrahedron*, **24**, 4249 (1968).

(18) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

(19) B. Holmberg, *Chem. Ber.*, **45**, 2997 (1912).

Communications to the Editor

Activation through Impregnation. Permanganate-Coated Solid Supports[1]

Sir:

Although potassium permanganate is a powerful oxidizing agent, its utility in organic synthesis has been severely limited by solubility problems.[2] One recent development that has significantly expanded the scope of this reagent was the demonstration that $KMnO_4$ forms a stable complex with dicyclohexyl-18-crown-6 which is soluble in benzene and reactive toward a variety of organic substrates.[3] In the absence of the crown ether, potassium permanganate has no detectable solubility in benzene and is unreactive.

We have discovered that potassium permanganate can be activated for certain oxidations in benzene by the very simple process of impregnation onto inorganic supports such as Linde Molecular Sieves, silica gel, and certain clays and now wish to report preliminary results obtained for alcohol oxidations. The following procedure has been used to prepare sieve/$KMnO_4$ reagents. A 2-L round-bottomed flask was charged with 500 mL of 0.06 M aqueous potassium permanganate and 20 g of Linde 13X Molecular Sieves ($\frac{1}{16}$-in. pellets)[4] was added to it in one portion.[5] The flask was then transferred to a rotary evaporator and water was removed under reduced pressure.[6] The coated pellets were separated physically from nonadsorbed potassium permanganate by screening (20 mesh). Analysis of the reagent revealed a loading of 0.27 mmol of $KMnO_4$/g of reagent.[7]

When 15.0 g of sieve/$KMnO_4$ was suspended in 20 mL of freshly distilled benzene containing 0.250 g (1.36 mmol) of cyclododecanol and the resulting mixture heated to 70 °C for 1.5 h, analysis of the liquid phase by GLC indicated complete conversion to cyclododecanone. The ketone was isolated by filtering the product mixture through Celite, washing the pellets with 70 mL of benzene, and removing the solvent from the combined filtrate under reduced pressure yielding 0.226 g (90%) of cyclododecanone as a colorless solid which melted at 56–59 °C.[8] The infrared and NMR spectra were identical with those of an authentic sample. Control experiments carried out in which sieve/$KMnO_4$ was replaced by either reagent grade potassium permanganate[9] or an aqueous potassium permanganate solution (organic–aqueous phase oxidation) showed no loss of alcohol in the organic phase after heating for 50 h at 70 °C. We have also found that potassium permanganate can be activated by impregnation onto various other supports; our results are summarized in Table I.[10]

Most of our work has been done with molecular sieves in pelleted form in order that nonadsorbed permanganate could be removed and thereby make analysis of loading and reactivity possible. Comparison of loading with oxidizing capacity for reagents **1–6** indicates reasonably efficient utilization of impregnated permanganate.[11] On the basis of loading, oxidizing capacity, and reactivity, Linde 13X Molecular Sieves ($\frac{1}{16}$-in. pellets) appear optimal as a support system. Other useful reagents which were derived from inorganic support material but which could not be analyzed for adsorbed permanganate are listed in Table I (reagents **7–11**).

Further examples of oxidations by a sieve/$KMnO_4$ are illustrated in Table II. In general, high yields of ketones and modest yields of aldehydes can be obtained.[12] Although we are still exploring the scope of sieve/$KMnO_4$-based oxidations, our results thus far indicate the above procedure to be com-

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.[7] [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 KMnO$_4$ 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/KMnO$_4$ 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-cyanooctane.[14] Attempted reaction of sodium cyanide pellets or aqueous sodium cyanide solution with 1-bromooctane in benzene under similar conditions gave no detectable 1-cyanooctane. 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 transfer[15] and triphase catalysis.[16,17]

References and Notes

(1) This work was supported by the National Science Foundation Grant No. MPS74-23925 and the donors of the Petroleum Research Fund, administered by the American Chemical Society.
(2) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 257–291.
(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/ KMnO$_4$ 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 KMnO$_4$/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 KMnO$_4$ 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 MnO$_2$) is not presently clear.
(12) Aldehydes formed in these reactions undergo further oxidation to the corresponding carboxylic acid.
(13) G. Cainelli, G. Cardillo, M. Orena, and S. Sandri, J. Am. Chem. Soc., 98, 6737 (1976); K. B. Sharpless and K. Akashi, ibid., 98, 1986 (1976); E. J. Corey and C. U. Kim, ibid., 94, 7586 (1972); E. J. Corey and J. W. Suggs, Tetrahedron Lett., 2647 (1975); R. Ratcliffe and R. Robertson, J. Org. Chem., 35, 4000 (1970); S. L. Regen, J. Cella and J. P. McGrath, Tetrahedron Lett., 4115 (1975).
(14) Unpublished observations by S. L. Regen and S. J. Liaw.
(15) J. Dockx, Synthesis, 441 (1973); E. V. Dehmlow, Angew. Chem., Int. Ed. Engl., 13, 170 (1974); E. V. Dehmlow, Chem. Technol., 210 (1975).
(16) S. L. Regen, J. Am. Chem. Soc., 97, 5956 (1975); S. L. Regen, ibid., 98, 6270 (1976); S. L. Regen and L. Dulak, ibid., in press; S. L. Regen, J. Org. Chem., in press; J. M. Brown and J. A. Jenkins, J. Chem. Soc., Chem. Commun., 458 (1976); M. Cinouini, S. Colonna, H. Molinari, and F. Montanri, ibid., 394 (1976).
(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.

Steven L. Regen,* Chitra Koteel

Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233

Microenvironment within a Solid-Phase Cosolvent[1]

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-