analogy to the case of DBH vs. DBO,[1] the highly efficient, temperature-independent photolysis of **2** is attributed to its rigidity and to its >12 kcal mol^{-1} higher singlet energy than **1**. Finally, we note that **18** shows a high Φ_r despite its high E_a^*. Although this anomalous behavior suggests an unusually large Arrhenius *A* factor for decomposition of A^{*1}, few *A* factors for excited-state reactions are presently available, let alone interpretable.[40]

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References and Notes

(1) P. S. Engel and C. Steel, *Acc. Chem. Res.*, **6,** 275 (1973).
(2) H. Dürr and B. Ruge, *Top. Curr. Chem.*, **66,** 53 (1976).
(3) P. S. Engel, R. A. Hayes, L. Keifer, S. Szilagyi, and J. W. Timberlake, *J. Am. Chem. Soc.*, **100,** 1876 (1978).
(4) W. D. K. Clark and C. Steel, *J. Am. Chem. Soc.*, **93,** 6347 (1971).
(5) C. Steel, *J. Phys. Chem.*, **67,** 1779 (1963).
(6) DBO = 2,3-diazabicyclo[2.2.2]oct-2-ene; DBH = 2,3-diazabicyclo[2.2.1]hept-2-ene.
(7) N. J. Turro, K. C. Liu, W. Cherry, J. M. Liu, and B. Jacobson, *Tetrahedron Lett.*, 555 (1978).
(8) J. A. Berson and R. F. Davis, *J. Am. Chem. Soc.*, **94,** 3658 (1972).
(9) J. P. Snyder, *Diss. Abstr.*, **26,** 5728 (1966).
(10) E. L. Allred and B. R. Beck, *Tetrahedron Lett.*, 437 (1974).
(11) N. J. Turro, C. A. Renner, W. H. Waddell, and T. J. Katz, *J. Am. Chem. Soc.*, **98,** 4320 (1976).
(12) P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, **97,** 6754 (1975).
(13) J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.*, **92,** 1086 (1970).
(14) E. L. Allred and K. J. Voorhees, *J. Am. Chem. Soc.*, **95,** 620 (1973). The authors are grateful to Professor Allred for the NMR spectrum of **10.**
(15) M. J. Mirbach, K. C. Liu, M. F. Mirbach, W. R. Cherry, N. J. Turro, and P. S. Engel, *J. Am. Chem. Soc.*, **100,** 5122 (1978).
(16) P. S. Engel, R. L. Allgren, W. K. Chae, R. A. Leckonby, and N. A. Marron, *J. Org. Chem.*, in press.
(17) W. R. Roth and G. Erker, *Angew. Chem.*, **85,** 510 (1973).
(18) J. P. Snyder and D. N. Harpp, *J. Am. Chem. Soc.*, **98,** 7821 (1976).
(19) Good single exponential decay was observed from DBO and **11**. Most of the (weak) emission from **12** corresponded to τ_f = 0.5 ns, but an even weaker tail of $\tau_f \sim$ 3 ns was also seen. The latter is assumed to arise from an impurity.
(20) C. C. Wamser, R. T. Medary, I. E. Kochevar, N. J. Turro, and P. L. Chang, *J. Am. Chem. Soc.*, **97,** 4864 (1975).
(21) M. J. Mirbach, M. F. Mirbach, W. R. Cherry, N. J. Turro, and P. S. Engel, *Chem. Phys. Lett.*, **53,** 266 (1978).
(22) M. Martin and W. R. Roth, *Chem. Ber.*, **102,** 811 (1969).
(23) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5345 (1969).
(24) L. A. Paquette and L. M. Leichter, *J. Org. Chem.*, **39,** 461 (1974).
(25) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341 (1969).
(26) H. D. Martin, B. Heiser, and M. Kunze, *Angew. Chem., Int. Ed. Engl.*, **17,** 696 (1978).
(27) In contrast to the literature results with DBO,[4] irradiation of **10** and **11** to >25% conversion in benzene gave a quantitative yield of nitrogen.
(28) H. D. Fühlhuber, C. Gousetis, T. Troll, and J. Sauer, *Tetrahedron Lett.*, 3903 (1978).
(29) L. A. Paquette and M. J. Epstein, *J. Am. Chem. Soc.*, **95,** 6717 (1973).
(30) M. F. Mirbach, M. J. Mirbach, K. C. Liu, and N. J. Turro, *J. Photochem.*, **8,** 299 (1978).
(31) This scheme is well supported in compounds closely analogous to **18.**[32]
(32) S. D. Andrews and A. C. Day, *J. Chem. Soc. B.*, 1271 (1968).
(33) The value of E_a^* was actually given[30] as 6.5 kcal mol^{-1}, but, in view of the obvious curvature in the published graph, we used the fluorescence data to plot $\ln[\Phi_r^{-1} - c]$ vs. T^{-1}. The value of *c* which gave the most linear plot was 2.4, in reasonable agreement with that calculated from $c = (1 - \Phi_r)/\Phi_f$.
(34) P. Dowd, *J. Am. Chem. Soc.*, **88,** 2587 (1966); P. Dowd and K. Sachdev, *ibid.*, **89,** 715 (1967).
(35) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **101,** 4688 (1979).
(36) P. S. Engel, D. J. Bishop, and M. A. Page, *J. Am. Chem. Soc.*, **100,** 7009 (1978).
(37) B. Bigot, A. Sevin, and A. Devaquet, *J. Am. Chem. Soc.*, **100,** 2639 (1978).
(38) Since the diagram for two-bond cleavage correlates diimide with $N_2 + H_2$, applying it to radical formation seems unjustified. Furthermore, it is not clear what effect the cyclopropane ring in **14** has on the potential energy curves.
(39) Attempts to detect *trans*-**1** by matrix isolation IR have been unsuccessful. We thank Professor Orville Chapman and Mr. Richard Hayes for carrying out these experiments.
(40) For other examples of temperature-dependent solution phase photoreactions, see ref 30; T. W. Knittel, G. Fischer, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1930 (1974); M. V. Encina and E. A. Lissi, *J. Photochem.*, **6,** 173 (1976); D. S. Weiss, *Mol. Photochem.*, **8,** 477 (1977).

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One-Electron Oxidation of Vinylidene–Carbene Complexes of Iron Porphyrins. Isolation of Complexes Spectrally Analogous to Catalase and Horseradish Peroxidase Compounds I

Sir:

The reactions of catalases and peroxidases with various two-electron oxidants lead to intermediate iron complexes, called compounds I and II, which retain, respectively, 2 and 1 oxidizing equiv above the native Fe(III) hemoprotein.[1] The knowledge of the structure and reactivity of these intermediates appears especially important since they play a key role in the catalytic function of the corresponding hemoproteins. From their spectroscopic properties,[2] compounds II of catalase and peroxidases are generally believed to be porphyrin–iron(IV) complexes with an oxygenated exogenous ligand which could be an oxo or an OH ligand. The structures of compounds I, which could be considered formally as iron(V) porphyrin complexes, are even less clear. Cytochrome *c* peroxidase compound I has been depicted as an iron(IV) porphyrin complex with a free radical of an amino acid residue in the vicinity of the heme iron.[3] Horseradish peroxidase (HRP) and catalase (CAT) compounds I have been described as iron(IV) [porphyrin π cation radical] complexes, because of their abnormal electronic absorption spectra which resemble those of magnesium, nickel, or cobalt porphyrin π cation radicals.[4] Iron porphyrin π cation radicals[5] have also been proposed as intermediates in electron transfers by cytochromes.[4d-f]

The carbon analogues of porphyrin–iron oxo species, porphyrin–iron(IV)=O, possibly present in CAT and HRP compounds II, are the carbene complexes [porphyrin–iron(II)←CRR′], which can be considered, at least formally,[6] as [porphyrin–iron(IV)=CRR′] complexes. Evidence has been presented in favor of the involvement of such cytochrome P450–carbene complexes,[7] and we have isolated a number of stable iron porphyrin–carbene complexes.[8] The latter exhibit visible spectra quite similar to those of compounds II but are considerably more stable. We thus could expect that their one-electron oxidation would lead to iron porphyrin complexes analogous to HRP and catalase compounds I, but also more stable. The present paper describes the preparation of stable iron porphyrin complexes from the one-electron oxidation of the vinylidene–carbene complexes Fe[porphyrin][$C{=}C(p\text{-}ClC_6H_4)_2$][8c] by ferric or cupric chloride, which exhibit visible spectra similar to those of catalase or HRP compounds I.

As shown in Figure 1a, the progressive addition of 1 equiv of $CuCl_2$ in acetonitrile to a benzenic solution of complex **1**, Fe[TPP[9]][$C{=}C(p\text{-}ClC_6H_4)_2$],[8c] leads to a gradual transformation, with isobestic points at 377, 430, 521 and 557 nm, of the characteristic visible spectrum of complex **1** into that of a new complex, **2**. In a typical preparative experiment, complex **2** was obtained from reaction of complex **1** (10^{-4} M in benzene) with 1 equiv of $FeCl_3$ (10^{-1} M in acetonitrile, added progressively within 5 h), followed by solvent evaporation, column chromatography on silica gel (elution with benzene and benzene-acetone (70:30) affording respectively un-

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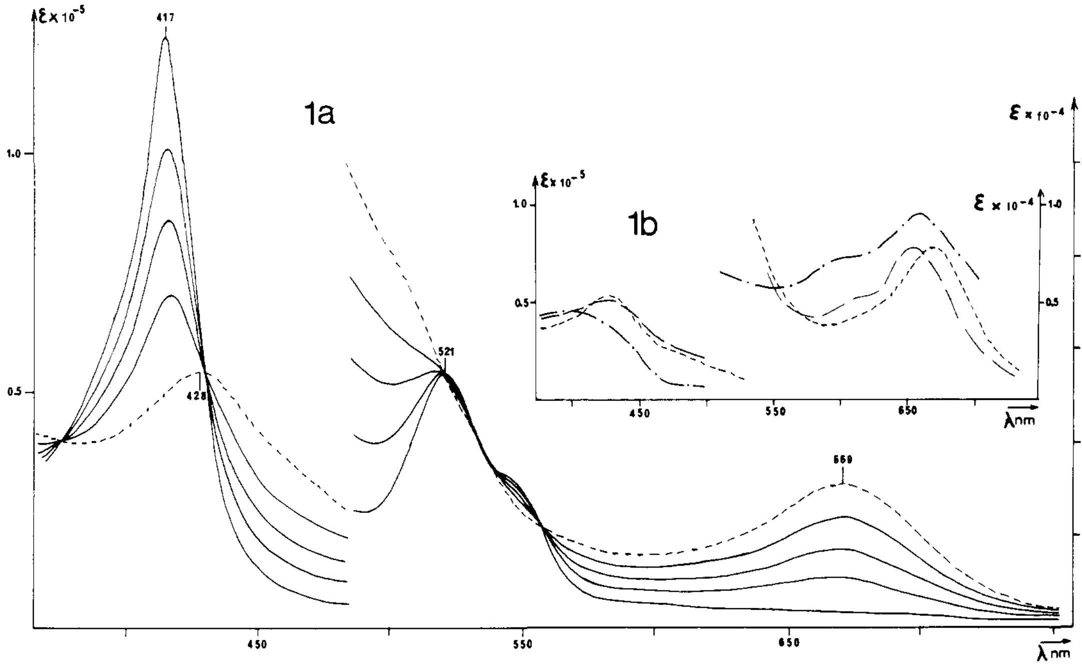


Figure 1. (1a) Oxidation of complex **1** (0.1 mM in C_6H_6) by increasing amounts of $CuCl_2$ in CH_3CN, followed by visible spectroscopy: (—) complex **1** and successive additions of 0.25 equiv of $CuCl_2$ and recording of the spectra after ~0.5 h (- - -) of complex **2** obtained after addition of 1 equiv of $CuCl_2$. (1b) Comparison of the spectra of complex **2** (- - -), **2‴** (— —) and of CAT compound I (— • —).

reacted complex **1** and complex **2**), and crystallization from acetone-hexane. Black shiny crystals of complex **2** (80% yield) were obtained: λ (ε) 428 (5.4 × 10^4) and 669 nm (7.8 × 10^3) in benzene.

The following data indicate that complex **2** derives from complex **1** only by a one-electron oxidation and a chloride transfer. In mass spectrometry (70 eV, 10^{-6} mmHg), both complexes decompose at ~70 °C with the appearance of an intense peak with an isotopic cluster characteristic of the presence of two chlorine atoms at *m/e* 246 (for ^{35}Cl), indicative of the ion corresponding to the vinylidene-carbene $C{=}CR_2$ or its rearranged product $RC{\equiv}CR$ (R = p-ClC_6H_4). The elemental analysis of complex **2** (C, H, N, Cl) corresponds to the formula $Fe(TPP)(C_{14}H_8Cl_2)(Cl)$. Reduction of complex **2** by sodium dithionite (C_6H_6-H_2O) or iron powder (CH_2Cl_2-MeOH) leads quantitatively to complex **1**. Titration of complex **1** by $CuCl_2$ or $FeCl_3$ indicates that 1 oxidizing equiv is necessary for the complete formation of complex **2**.[10] Moreover, the thermal decomposition of complex **2** in a sealed tube (150 °C, 10^{-2} mmHg) leads quantitatively to Fe^{III}[TPP][Cl] and $RC{\equiv}CR$ (R = p-ClC_6H_4). In complex **2**, one chloride is present as a counterion or iron ligand since it can be replaced by other anions (X^- = ClO_4^-, Br^-, F^-) upon treatment of complex **2** in C_6H_6 by $AgClO_4$ and the X^- anion (H_2O, 1 M NaX, 10^{-2} M HX). The corresponding new entities **2′** (X = ClO_4), **2″** (X = Br), and **2‴** (X = F) exhibit visible spectra similar to that of complex **2**: **2′**, λ (ε) 410 (4.8 × 10^4), 673 nm (5.8 × 10^3); **2″**, 432 (5.1 × 10^4), 676 (7.4 × 10^3); **2‴**, 427 (5.3 × 10^4), 654 (8.0 × 10^3) (in C_6H_6). Complexes **2**, **2′**, and **2″** can be equally obtained by oxidation of complex **1**, respectively, by Cl_2, $Fe(ClO_4)_3$, and Br_2.

All of the above data are in agreement with the formula Fe[TPP][$C{=}C(p$-$ClC_6H_4)_2$][Cl] for complex **2**. More generally, analogues of complex **2**[11] are obtained upon $FeCl_3$ (or $CuCl_2$) oxidation of the vinylidene-carbene complexes of various iron porphyrins, Fe[porphyrin][$C{=}C(p$-$ClC_6H_4)_2$] (porphyrin = OEP, DPDME, and PPIX[9]).

The main characteristic of complex **2**, and its analogues with various porphyrins, is their peculiar electronic spectra with a weak and broad Soret peak and a visible part (500–700 nm) involving either a peak at ~670 nm (complex **2**) or a broad absorption without any well-defined peak (OEP, DPDME, and PPIX complexes[11]). Such characteristics have been already reported for π cation radicals of porphyrin complexes of several metals not including iron.[4]

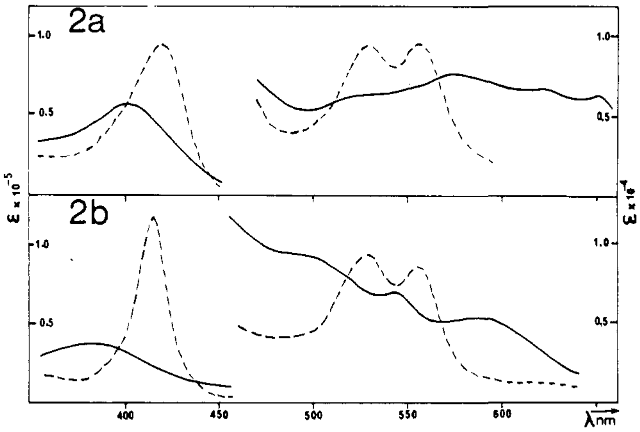
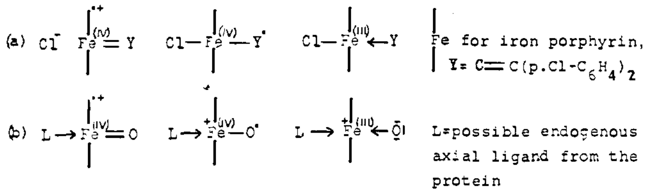


Figure 2. Comparison between the electronic spectra of HRP compounds II (2a, - - -) and I (2a, —) and those of the complexes Fe[DPDME]-[$C{=}C(p$-$ClC_6H_4)_2$][*N*-methylimidazole] (2b, - - -) and Fe[DPDME]-[$C{=}C(p$-$ClC_6H_4)_2$][Cl] (2b, —).

As shown in Figure 1b, there is a strong similarity between the electronic spectra of complexes **2** and **2‴** and that of catalase compound I.[12] The electronic spectra of the OEP, DPDME, and PPIX complexes[11] rather resemble that of HRP compound I. Figure 2 underlines the analogy between the electronic spectra of HRP compounds II and I and, respectively, of the complexes Fe[DPDME][$C{=}C(p$-$ClC_6H_4)_2$]-[*N*-methylimidazole][15] and Fe[DPDME][$C{=}C(p$-$ClC_6H_4)_2$][Cl].

The above results suggest a common formulation [porphyrin-Fe=Y]$^{+\cdot}$ for complex **2** and its analogues with other porphyrins (Y = $C{=}C(p$-$ClC_6H_4)_2$) and for CAT and HRP compounds I (Y = O). More detailed studies are still necessary to precisely determine the electronic structure of these com-

Scheme I. Possible Structures for Complex **2** (a) and for CAT and HRP Compounds I (b)



plexes[12] (Scheme I) which should depend upon the nature of Y, the porphyrin,[14] the possible second axial ligand of iron, and the heme environment.

References and Notes

(1) (a) H. B. Dunford and J. S. Stillman, *Coord. Chem. Rev.*, **19**, 187 (1976); (b) T. Yonetani, *Adv. Enzymol.*, **33**, 309 (1970); I. Yamasaki, in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, 1974, p 535.

(2) (a) T. Moss, A. Ehrenberg, and A. J. Beorden, *Biochemistry*, **8**, 4151 (1969); (b) T. Harami, Y. Maeda, U. Morita, A. Trautwein, and U. Gonser, *J. Chem. Phys.*, **67**, 1164 (1977); (c) G. Rakhit, T. G. Spiro, and M. Ueda, *Biochem. Biophys. Res. Commun.*, **71**, 803 (1976); (d) R. H. Felton, A. Y. Romans, Nai-Teng Yu, and G. R. Schonbaum, *Biochim. Biophys. Acta*, **434**, 82 (1976).

(3) (a) T. Yonetani, H. Schleyer, and A. Ehrenberg, *J. Biol. Chem.*, **241**, 3240 (1966); (b) T. Yonetani and A. F. W. Coulson, *Biochemistry*, **14**, 2389 (1975).

(4) (a) D. Dolphin, A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 614 (1971); (b) D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer, and R. H. Felton, *Ann. N.Y. Acad. Sci. U.S.A.*, **206**, 177 (1973); (c) R. H. Felton, G. S. Owen, D. Dolphin, A. Forman, D. G. Borg, and J. Fajer, *ibid.*, **206**, 504 (1973); (d) D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, **7**, 26 (1974); (e) D. Dolphin, T. Niem, R. H. Felton, and S. Fujita, *J. Am. Chem. Soc.*, **97**, 5288 (1975); (f) E. G. Johnson, T. Niem, and D. Dolphin, *Can. J. Chem.*, **56**, 1381 (1978).

(5) Very recently, it has been shown that the chemical oxidation of the iron(II)[benzporphyrin][CO][pyridine] complex leads to the corresponding ferrous benzoporphyrin π cation radical: A. Vogler, B. Rethwisch, H. Kunkely, and J. Hütterman, *Angew. Chem., Int. Ed. Engl.*, **17**, 952 (1978). This reaction occurs because of the remarkably low oxidation potential of the benzporphyrinic ligand which is below that of iron(II). For other iron porphyrin complexes, Fe^{III}[TPP][Cl] or $(Fe^{III}[TPP])_2O$, electrochemical oxidation has given Fe(IV) complexes whose further oxidation has led to highly unstable species and irreversible modification of the porphyrin ring.[4c]

(6) In the following, the complexes iron[porphyrin][Y] with Y = O or CRR′ are most often written formally $Fe^{IV}{=}Y$. They may also be written $Fe^{III}{-}Y\cdot$ or $Fe^{II}{\leftarrow}Y$ (the involvement of an oxenoid form $Fe^{II}{\leftarrow}\underline{O}|$ has been invoked: G. A. Hamilton in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, 1974, p 405).

(7) (a) D. Mansuy, W. Nastainczyk, and V. Ullrich, *Naunyn-Schmiedebergs Arch. Pharmakol. Exp. Pathol.*, **285**, 315 (1974); (b) C. R. Wolf, D. Mansuy, W. Nastainczyk, G. Deutschmann, and V. Ullrich, *Mol. Pharmacol.*, **13**, 698 (1977).

(8) (a) D. Mansuy, M. Lange, J.-C. Chottard, P. Guérin, P. Morlière, D. Brault, and M. Rougee, *J. Chem. Soc., Chem. Commun.*, 648 (1977); (b) D. Mansuy, M. Lange, J. C. Chottard, J. F. Bartoli, B. Chevrier, and R. Weiss, *Angew. Chem., Int. Ed. Engl.*, **17**, 781 (1978); (c) D. Mansuy, M. Lange, and J. C. Chottard, *J. Am. Chem. Soc.*, **100**, 3214 (1978); (d) D. Mansuy, P. Guérin, and J. C. Chottard, *J. Organomet. Chem.*, **171**, 195 (1979).

(9) Used abbreviations: TPP, OEP, DPDME, and PPIX = respectively the dianions of *meso*-tetraphenylporphyrin, octaethylporphyrin, deuteroporphyrin IX dimethyl ester, and protoporphyrin IX.

(10) Addition of an excess of oxidant ($FeCl_3$ or $CuCl_2$) to a solution of complex **1** gives a new compound (λ (ϵ) 430 (1.4×10^5), 509 (7.7×10^3), 549 (12.0×10^3), 585 (15.5×10^3) and 631 nm (7.1×10^3) in benzene), which cannot be reduced back to complexes **2** or **1**. Preliminary electrochemical studies confirm that the first one-electron oxidation of complex **1** leads to complex **2** (D. Lexa and J. M. Saveant, unpublished results).

(11) λ (ϵ): OEP complex, 382 (4.5×10^4), 497 (9.8×10^3), and 593 nm (5.8×10^3) in benzene; DPDME complex, 382 (3.5×10^4), 498 (9.3×10^3), 542 (6.9×10^3), and 588 (5.3×10^3) in benzene; PPIX complex, ~500 (8×10^3) and 600 (5×10^3) in DMF. As complex **2**, these compounds can be reduced back to the starting iron[porphyrin][$C{=}C(p\text{-}ClC_6H_4)_2$] complexes by sodium dithionite or iron powder.

(12) (a) Complex **2** and catalase compound I also display a paramagnetism of the same magnitude, at room temperature: $\mu_2 = 3.7$[13a] and $\mu_{CAT\ I} = 3.9\ \mu_B$.[13b] Preliminary ESR studies indicate that complex **2** (5×10^{-2} M in toluene) shows no signal at 298 K and broad signals at $g = 4.4$ and 2.03 at 77 K. Similar spectra have been described for the iron(III)[TPP][ClO_4] (solid sample, $g = 4.75$ and 2.03 at 10 K: T. Mashiko, M. E. Kastner, K. Spartalian, W. R. Scheidt, and C. A. Reed, *J. Am. Chem. Soc.*, **100**, 6354 (1978)) and iron(III)[OEP][ClO_4] (solid sample, g values of approximately 4 and 2 at 78 K: D. H. Dolphin, J. R. Sams, and Tsang Bik Tsin, *Inorg. Chem.*, **16**, 711 (1977)) complexes. (b) Recent ^1H NMR data for HRP compound I do not seem in favor of the iron(IV)[porphyrin π cation radical] structure: I. Morishima and S. Ogawa, *J. Am. Chem. Soc.*, **100**, 7125 (1978).

(13) (a) Measured by the Evans' method: D. F. Evans, *Chem. Commun.*, 2003 (1959); (b) A. S. Brill in "Comprehensive Biochemistry", Vol. 14, M. Florkin and E. H. Stotz, Eds., Elsevier, Amsterdam, 1966, p 464.

(14) R. K. DiNello and D. Dolphin, *Biochem. Biophys. Res. Commun.*, **86**, 190 (1979).

(15) *N*-Methylimidazole was added to the Fe[DPDME][$C{=}C(p\text{-}ClC_6H_4)_2$] complex to complete the coordination sphere of the iron and to account for the possible binding to iron of an axial ligand from the protein in HRP compound II.

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Reactions of Butane and Isobutane Catalyzed by Zirconium Oxide Treated with Sulfate Ion. Solid Superacid Catalyst[1]

Sir:

The synthesis of solid superacids as catalysts has been desired because of many advantages of solid catalyst. We have succeeded in synthesizing a solid superacid, not containing any halogen, which can be used at the high temperature up to 500 °C.

In the previous paper,[2] we reported that remarkable increases in the surface acidity and in the catalytic activity of Fe_2O_3 were caused by treatment with sulfate ion, followed by calcination, of $Fe(OH)_3$ or Fe_2O_3 prior to the crystallization. This preparation method of catalyst was applied to other metal oxides,[3] and zirconium oxide was found to show the exceedingly high surface acidity, much higher than that of SiO_2–Al_2O_3 which is well known as one of the solid acid catalysts with the highest surface acidity.[4] In the present work, we studied the catalytic action for reactions of saturated hydrocarbons which are generally catalyzed by strong acid, especially superacid such as SbF_5–HF and SbF_5–FSO_3H,[5] and found that the sulfate-treated zirconium oxide is catalytically active for the reactions of butane and isobutane, even at room temperature.

The catalyst was prepared as follows. $Zr(OH)_4$[6] was obtained by hydrolyzing $ZrOCl_2{\cdot}8H_2O$ with aqueous ammonium hydroxide, washing the precipitates, and drying them at 100 °C for 24 h. The treatment of catalyst with sulfate ion was performed by pouring 30 mL of 1 N H_2SO_4[7] into 2 g of the dried hydroxides on a filter paper. After drying, the materials were powdered below 100 mesh, calcined in a Pyrex tube in air at 500 °C for 3 h, and finally sealed in an ampule until use.

The catalyst prepared in the present manner[8] showed activity for the skeletal isomerization of butane at room temperature. When the reaction was carried out in a recirculation reactor having a volume of ~170 mL, 0.8 g of the catalyst and 10 mL (NTP) of butane being used, isobutane was produced in 7% yield for 48 h and 18% yield for 120 h.

Since the present catalyst is calcined at 500 °C,[9] and hence can be used up to 500 °C for reaction, the reaction was carried out at high temperature under the pulse reaction conditions, where the contact period is quite short. The reaction was carried out in a microcatalytic pulse reactor using a stainless tube with a fixed bed catalyst (flow rate of He for carrier gas, 3 mL/min; catalyst amount, 0.3 g; pulse size, 0.04 mL). The catalyst was held in place by a glass wool plug and heat treated at 400 °C for 1.5 h in the He flow before reaction. Gaseous reactants were introduced via a syringe pump and passed through the catalyst bed. Effluent products were directly introduced into a gas chromatographic column for analysis

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