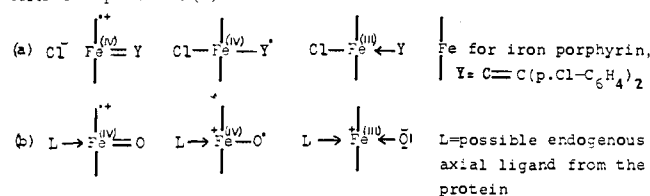


Scheme I. Possible Structures for Complex 2 (a) and for CAT and HRP Compounds I (b)



plexes¹² (Scheme I) which should depend upon the nature of Y, the porphyrin,¹⁴ the possible second axial ligand of iron, and the heme environment.

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- (10) Addition of an excess of oxidant (FeCl_3 or CuCl_2) to a solution of complex 1 gives a new compound (λ (e) 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studies confirm that the first one-electron oxidation of complex 1 leads to complex 2 (D. Lexa and J. M. Saveant, unpublished results).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 (e): 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][$\text{C}=\text{C}(\text{p}-\text{Cl}-\text{C}_6\text{H}_4)_2$] 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 $\mu_{\text{CAT I}} = 3.9 \mu_B$.^{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. Spatallan, 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).
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Reactions of Butane and Isobutane Catalyzed by Zirconium Oxide Treated with Sulfate Ion. Solid Superacid Catalyst¹

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 $\text{Fe}(\text{OH})_3$ 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 $\text{SiO}_2-\text{Al}_2\text{O}_3$ 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 $\text{SbF}_5-\text{FSO}_3\text{H}$,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. $\text{Zr}(\text{OH})_4$ ⁶ was obtained by hydrolyzing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 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 manner⁸ 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

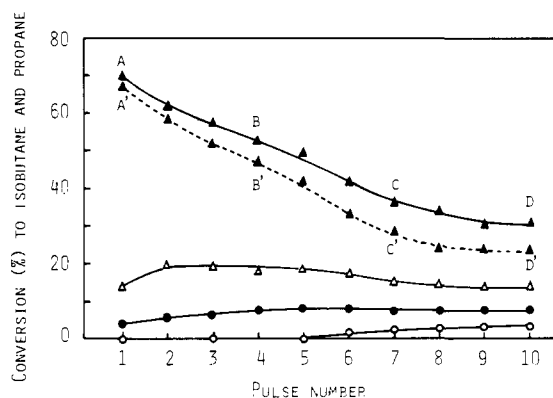


Figure 1. Reaction of butane: reaction temperatures, 100 (○), 120 (●), 150 (△), 250 °C (▲); yield of propane, A (35%), B (13%), C (5%), D (4%), A' (34%), B' (10%), C' (4%), D' (3%); isobutane only for the reactions at 100, 120, and 150 °C. - - -: reaction over the SO₂-treated catalyst, which was prepared by exposing Zr(OH)₄ to SO₂ for 10 min at room temperature and then calcining at 500 °C for 3 h.

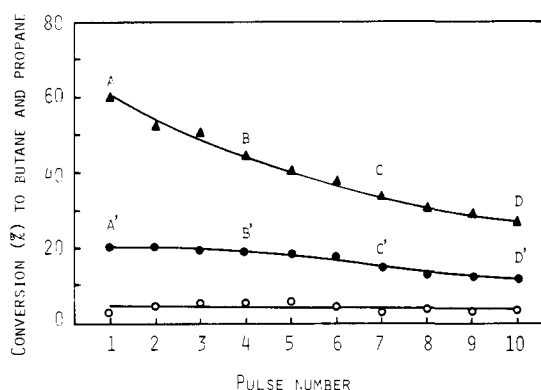


Figure 2. Reaction of isobutane: reaction temperature, 120 (○), 150 (●), 230 °C (▲); yield of propane, A (33%), B (13%), C (8%), D (5%), A' (3%), B' (2%), C' and D' (trace); butane only for the reaction at 120 °C.

(tricsesyl phosphate, 5 m, at room temperature). The percent conversion of reactants into products was obtained by estimating peak areas (corrected).

The conversions at various temperatures are shown as a function of pulse number in Figure 1. The catalyst showed activity at the reaction temperature of 100 °C, and the product was isobutane at 100, 120, and 150 °C of reaction. At 250 °C, propane was also produced in addition to isobutane.^{10,11} It is of interest that the treatment with SO₂ also enhanced the activity to the same extent as that with sulfuric acid.¹²

In Figure 2 are shown the reaction courses of isobutane at various temperatures. The product was butane at 120 °C and butane and propane at 150 and 230 °C. It is seen from Figures 1 and 2 that the catalyst kept its activity almost constant during reaction at below 150 °C.¹³ The continual loss of activity at 230 and 250 °C results from decrease of propane formed, the catalytic activity for the skeletal isomerization being constant. The active sites for formation of propane were probably poisoned at high temperatures of reaction, since the catalysts were colored, yellow, after reaction.

The SiO₂-Al₂O₃ catalysts¹⁴ were totally inactive even at temperature of 350 °C for both butane and isobutane. Acid strengths of SiO₂-Al₂O₃ used were in the range of $-12.70 < H_0 \leq -11.35$.¹⁵ Consequently, the present catalyst is considered to have a surface acidity higher than $H_0 = -12.70$. Since the acid stronger than $H_0 = -10.6$, which corresponds to the acid strength of 100% H₂SO₄, is known as superacid,¹⁶ the present catalyst would be a solid superacid.¹⁷

The acid strength of the catalyst was examined by the visual

color change method of the Hammett indicators,⁴ where indicator dissolved in solvent is added to the sample in powder form placed in nonpolar solvent, but the present catalyst (white color) was immediately colored in organic solvents, benzene, toluene, hexane, carbon tetrachloride, etc. However, sulfuryl chloride was found to be quite suitable solvent for the acid strength determination of this superacid catalyst.¹⁸ In this manner, the catalyst changed distinctly the basic form (colorless) of *p*-nitrochlorobenzene ($pK_a = -12.70$), *m*-nitrochlorobenzene (-13.16), and 2,4-dinitrotoluene (-13.75) to the conjugate acid form (yellow) and slightly the color of 2,4-dinitrofluorobenzene (-14.52), but did not change the color of 1,3,5-trinitrobenzene (-16.04). Thus, the acid strength of the present catalyst is estimated to be $-14.52 \leq H_0$.¹⁹

Attempts to support SbF₅ or TaF₅ on Al₂O₃, SiO₂, and graphite²⁰ have been made for the synthesis of solid superacids, but their acid strengths were not measured. The present catalyst is the strongest surface-acid system known.

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- (7) TGA data of the ZrO₂ catalyst treated with 1 N H₂SO₄ showed a weight decrease of 10 wt % at 550–800 °C, which was probably caused by the decomposition of sulfate on the surface to form SO₃. The catalysts treated with 0.1 and 0.5 N H₂SO₄ showed the same activities and SO₃ contents as those of the sample treated with 1 N H₂SO₄, though, in the case of Fe₂O₃, the materials treated with sulfate ion of different concentrations showed the different catalytic activities and SO₃ contents.²
- (8) The present material showed IR absorption bands at 980, 1040, 1130, and 1240 cm⁻¹, which are assigned to the bidentate sulfate coordinated to metal elements.²
- (9) The catalytic activity of the treated Zr(OH)₄ decreased on raising the calcination temperature, 600 to 700 °C, owing to the decomposition of sulfate. The heat treatment at 500 °C showed the maximum activity.
- (10) Two more catalysts were differently prepared, and their activities for the reaction of butane were examined. One was prepared by hydrolyzing ZrO(NO₃)₂·2H₂O with aqueous ammonium hydroxide, washing the precipitates, drying, treating with 1 N H₂SO₄, and finally calcining at 500 °C. Another was prepared by treating Zr(OH)₄ of Nakarai Chemicals, Ltd., with 1 N H₂SO₄ and calcining at 500 °C. The conversions of butane into isobutane and propane at 250 °C were 16 and 6% for the first and sixth pulse reactions, respectively, by the former catalyst and 14 and 5% by the latter one.
- (11) At 350 °C of reaction, methane and ethane were observed, together with propane and isobutane; i.e., 13, 11, 43, and 8% for methane, ethane, propane, and isobutane, respectively, in the first pulse reaction and 7, 6, 36, and 9% in the sixth pulse reaction.
- (12) The catalysts similarly treated with H₂S and SO₃ were inactive at 250 °C. In the case of treatment with 1 N (NH₄)₂SO₄, the conversion was just 1.4% at 250 °C for the first pulse reaction.
- (13) The activity was greatly dependent on the calcination temperature of the hydroxide before the treatment. Namely, the catalysts prepared by pre-calcining the zirconium hydroxide at 400, 450 and 500 °C, then treating each with 1 N H₂SO₄, and finally calcining at 500 °C gave 62, 9, and 6% conversions, respectively, for the first pulse reaction run at 250 °C. DTA of Zr(OH)₄ showed that this material crystallizes at 410 °C. Thus, the treatment with sulfate ion on the crystallized oxide is not effective as was observed in the case of Fe₂O₃.²
- (14) N631(L) of Nikki Chemical Co. (Al₂O₃, 15 wt %) and Shokubai Kasei Co. (Al₂O₃, 13 wt %). These were heat treated at 500 °C.
- (15) These catalysts changed the basic form (colorless) of the indicator (*p*-nitrotoluene) whose pK_a value was -11.35 to the conjugate acid form (yellow), but did not change the color of indicator *p*-nitrochlorobenzene ($pK_a = -12.70$). The indicators were adsorbed on the oxide surface in benzene.⁴
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- (18) Guaranteed grade sulfuryl chloride, Wako Pure Chemical Co., was dried over silica gel before use.
- (19) Examination of the acid strength of SiO₂-Al₂O₃ measured by use of sulfuryl chloride showed the same results as observations using benzene (ref 14). The vapor of 2,4-dinitrofluorobenzene was also adsorbed on the present catalyst surface in a vacuum apparatus at room temperature, and the color of the indicator changed distinctly to the conjugate acid form (yellow).

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On the Use of Tetrphenylborate as a Phase Transfer Agent for Acid Catalysis

Sir:

Phase transfer catalysis has proven a remarkably versatile technique for facilitation of reactions involving anions.¹ A recent communication on catalysis by sodium tetrphenylborate for the acid hydrolysis of an ester suggested the potential extension of the phase transfer approach to reactions involving cations.² We report here, however, that this intriguing potential remains to be demonstrated, for the initial observations are attributable to decomposition of the tetrphenylborate rather than hydrolysis of an ester.

In the previous study² the hydrolysis of *p*-nitrophenyl acetate was followed spectrophotometrically at 865 nm. In a two-phase cyclohexane-HCl (1.5 N) system no reaction was observed in 48 h at 25 °C in the absence of sodium tetrphenylborate, but with added NaBPh₄ a rapid color change occurs which was attributed to the hydrolysis of *p*-nitrophenyl acetate. Our attempts to extend this result, however, led quickly to the observation that the same color is produced at the same rate with or without the *p*-nitrophenyl acetate present.

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To a stirred solution of 222 mg of *p*-nitrophenyl acetate in 25 mL of cyclohexane was added 25 mL of 1.5 N HCl and 346 mg of sodium tetrphenylborate. A yellow orange color appeared within 30 s which reached maximum intensity in 3 min. In the control reaction containing no *p*-nitrophenyl acetate, the color change was identical. The UV-visible spectrum (Beckman Acta M-VI) of the control reaction showed a broad maximum at 408 nm; the sum of this spectrum with that of pure *p*-nitrophenyl acetate in cyclohexane reproduced identically the spectrum of the assumed hydrolysis reaction. The reactions with and without *p*-nitrophenyl acetate also showed no differences at 865 nm (Spectronic 20).

To confirm the stability of *p*-nitrophenyl acetate, the reaction was repeated on a slightly larger scale. The organic phase was separated after 15 min, washed with dilute bicarbonate, and evaporated to constant weight at high vacuum. From an initial 546 mg of *p*-nitrophenyl acetate was obtained 658 mg of a gummy solid which integrated for 80% *p*-nitrophenyl acetate by NMR.³ The amount of crude *p*-nitrophenyl acetate is thus ~96%; crystallization from cyclohexane gave an isolated recovery of 445 mg (81.5%).

The instability of tetrphenylborate to acid is well established.^{4,5} Our results indicate that acid decomposition of tetrphenylborate is significantly faster than hydrolysis of *p*-nitrophenyl acetate. The utility of tetrphenylborate as a proton phase transfer agent would thus appear limited; those substrates reactive enough to compete with the decomposition of tetrphenylborate are likely to be easily reacted by other means.⁶

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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- (3) The NMR spectrum of the crude material showed only aromatic protons and the methyl singlet at 2.4 ppm. The percentage of *p*-nitrophenyl acetate was calculated by assuming that the 20% excess aromatic area relative to the methyl area is proportional to the weight of impurities. To the extent that the percentage of hydrogen is greater in phenylboron derivatives than in *p*-nitroacetate, this assumption would underestimate the recovery of *p*-nitrophenyl acetate.
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- (6) Professor Armstrong has informed us that tetraphenylborate exhibits varying stability to metal ions and may facilitate certain reactions involving metal cations.

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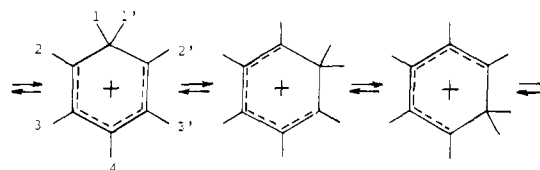
Elucidation of Chemical Exchange Networks by Two-Dimensional NMR Spectroscopy: The Heptamethylbenzenonium Ion

Sir:

For the investigation of chemical exchange processes, nuclear magnetic resonance (NMR) has proved to be a powerful and versatile technique. Much of the present detailed knowledge on chemical and biological rate processes is due to NMR investigations.^{1,2} Exchange processes have been studied by three types of techniques: (a) line-shape analysis,¹⁻⁵ (b) spin echo experiments,⁶ and (c) saturation transfer studies.⁷⁻¹⁰ These techniques, in particular (a) and (b), do not always lead to an intuitive grasp of the exchange network because the results are obtained through a computer least-squares fit.

We demonstrate in this letter a novel technique, recently proposed by Jeener,¹¹⁻¹³ which is based on the concept of two-dimensional (2D) spectroscopy.¹⁴⁻¹⁵ It leads to a particularly vivid representation of the exchange network ideally suited for a qualitative analysis of exchange networks by inspection.

We select as an example the well-investigated rearrangement of heptamethylbenzenonium ion.¹⁶⁻¹⁸ This ion undergoes an alkyl shift which makes all seven methyl groups equivalent at sufficiently high temperature:



There has been some discussion whether this shift is intramolecular involving either a 1-2 shift or a random shift with jumps, between all possible positions, or whether it is intermolecular. NMR line-shape analysis¹⁶ indicated in agreement with many further systems of similar structure² that the dynamics is governed by an intramolecular 1-2 methyl shift. Although the least-squares fit gives an unambiguous result, the visual evidence for this conclusion is just a slight line distortion for intermediate exchange rates.¹⁶ The mechanism has been verified also by a saturation transfer study.¹⁸

A two-dimensional exchange spectrum of heptamethylbenzenonium ion is shown in Figure 1. It can be interpreted as