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Hydrogenation of Fluoroolefins Studied by Gas Phase NMR: A New Technique for Heterogeneous Catalysis[†]

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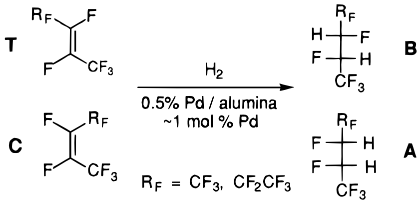
We report the first use of gas phase NMR to follow the kinetics of a heterogeneously catalyzed chemical process. Although one of the very first NMR experiments was carried out 50 years ago on hydrogen gas,[1] the subsequent development of nuclear magnetic resonance was largely concerned with condensed phases of matter. There exists, nevertheless, a substantial literature on gas-phase NMR dealing predominantly with physical studies.[2] The more chemically oriented work focused mostly on molecular conformational dynamics, isomerizations, and chemical equilibria involving, for example, hydrogen bonding.[3] We find that gas phase NMR has been surprisingly overlooked as a very useful technique to follow the reaction kinetics of volatile reactants in the presence or absence of catalysts.[4]

We applied this technique to the vapor phase hydrogenation of *cis*/*trans* mixtures of perfluoro-2-butenes and perfluoro-2-pentenes over palladium supported on alumina (eq 1).[5] We are focusing on reactions of organofluorine compounds mainly because the wide range of their ^{19}F NMR chemical shifts compensates for the broader line widths observed in the gas phase due to spin-rotation relaxation.[2] Moreover, a variety of such compounds are important in the production of replacements for ozone-depleting chlorofluorocarbons as refrigerants, propellants, fire extinguishants, and cleaning agents, but much remains to be learned about their chemistry wherein heterogeneous vapor phase manufacturing processes often lack fundamental understanding.[6]



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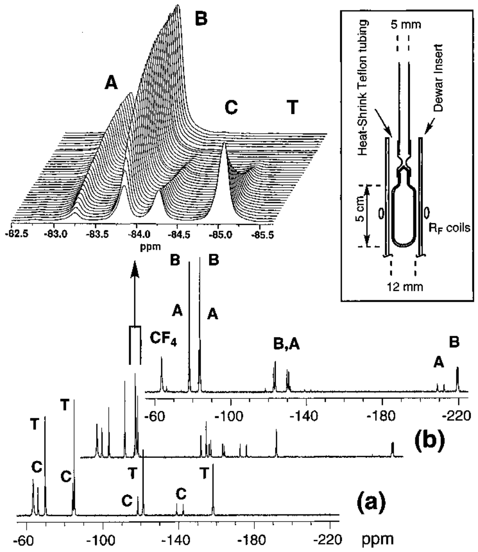

Figure 1. ^{19}F gas phase NMR spectra at three reaction times in the Pd/Al_2O_3-catalyzed hydrogenation of a 24.8:75.2% *cis*/*trans* mixture of perfluoro-2-pentenes at 65 °C (a) at the start, (b) at an intermediate time, and (c) at the end of the reaction. The stack plot in the upper left corner shows the partial time evolution of the CF_3 fluorine resonances (expansion of the spectral region indicated by the "tuning fork") of the perfluoroethyl groups of reaction components **C**, **T**, **A**, and **B** (see eq 1). Also shown is the reaction ampule in the Dewar insert of the NMR spectrometer.

We show that these hydrogenations are stereospecific, the *cis* olefin **C** giving the *erythro* hydrofluorocarbon (HFC) **A** and the *trans* olefin **T** giving the *threo* HFC **B**, assuming *cis* addition of dihydrogen to the double bond in common with the hydrogenations of hydrocarbon olefins.[7] In sharp contrast to the latter, there is no concomitant isomerization of the fluoroolefins over palladium, and *the trans olefin hydrogenates faster than the cis olefin*. We conclude that gas phase NMR appears to be a powerful new technique for heterogeneous catalysis that is particularly well suited for measurements of *relative rates* in competition studies.

The NMR reaction vessel is an ampule made from a short section (~5 cm) of a 12 mm NMR tube with a coaxial 5 mm tube extension to allow easy attachment to a vacuum system. The fluoroolefins are condensed into the evacuated NMR ampule, which contains the catalyst. A small amount of inert CF_4 is introduced as both a concentration and chemical shift standard. The 5 mm tube extension is sealed off with the ampule totally immersed in liquid nitrogen and containing a known pressure of hydrogen. The 5 mm stub serves to attach the ampule to a 5 mm NMR tube with a short piece of heat-shrink Teflon tubing (Figure 1) to facilitate its insertion into the spectrometer probe held at the desired temperature. The automated NMR data acquisition starts according to a script that defines the time steps in the repetitive spectral sampling.[8]

[†] Contribution number 7448.

[1] Purcell, E. M.; Pound, R. V.; Bloembergen, N. *Phys. Rev.* **1946**, *70*, 986.

[2] For reviews, see: (a) Govil, G. *Appl. Spectrosc. Rev.* **1973**, *7*, 47. (b) Armstrong, R. L. *Magn. Reson. Rev.* **1987**, *12*, 91. (c) Jameson, C. J. *Chem. Rev.* **1991**, *91*, 1375.

[3] For example, see: (a) Bauer, S. H.; True, N. S. *J. Chem. Phys.* **1980**, *84*, 2507. (b) Ross, B. D.; True, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 4871. (c) Spring, C. A.; True, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 7231. (d) Govil, G.; Clague, A. D. H.; Bernstein, H. J. *J. Chem. Phys.* **1968**, *49*, 2821. (e) Harris, R. K.; Rao, R. C. *Org. Magn. Reson.* **1983**, *21*, 580. (f) Hirano, T.; Miyajima, T. *J. Mol. Struct.* **1985**, *126*, 141.

[4] We were able to find only one paper in which NMR was used to study the kinetics of a chemical reaction in the gas phase: Haugh, M. J.; Dalton, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 5674.

[5] (a) Krespan, C. G. in *Chemistry of Organic Fluorine Compounds II. A Critical Review*; Hudlicky, M., Pavlath, A. E., Eds.; ACS Monograph 187; American Chemical Society: Washington, DC, 1995. (b) Krespan, C. G.; Rao, V. N. M. *U.S. Pat.* 5,171,902, 1992. (c) Rao, V. N. M.; Weigert, F. J.; Krespan, C. G. *U.S. Pat.* 5,268,122, 1993. (d) Seki, E.; Aoyama, H. *Kokai Pat. Hei* 5(1993)-140009. (e) Hudlicky, T.; Fan, R.; Reed, J. W.; Carver, D. R.; Hudlicky, M. *J. Fluorine Chem.* **1992**, *59*, 9. (f) Bispen, T. A.; Borutskaya, G. V.; Mikhailova, T. V.; Moldavskii, D. D.; Furin, G. G. *Zh. Prikl. Khim.* **1995**, *68*, 793.

[6] (a) Manzer, L. E.; Rao, V. N. M. *Adv. Catal.* **1993**, *39*, 328. (b) Rao, V. N. M. In *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994.

[7] For a review, see for example: Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*; Wiley: New York, 1993; pp 446−452.

[8] Gases are metered by filling a known volume with the appropriate pressure measured with a capacitance manometer. The approximate hydrogen pressure in the ampule at room temperature is calculated from $P_{298K} = (P_{77K}298)/77$. The commercial catalyst is 0.5% palladium on γ-alumina beads of 1.6 mm diameter (Engelhard, Inc.) freshly activated with hydrogen and vacuum treatments at elevated temperatures. The ampules are kept in liquid nitrogen until the start of the kinetic experiment. The spectra are recorded with a GE NMR Instruments Omega 360 spectrometer using a SunOS Release 4.03e operating system based on a Sun Sparc-1 computer. No field lock is used, and the ampules are not spun.

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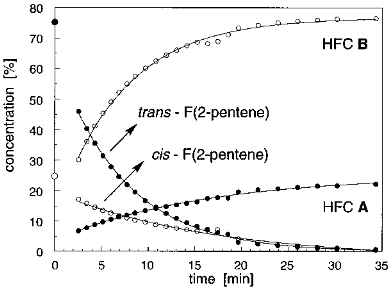

Figure 2. Kinetic plot for the Pd/Al_2O_3-catalyzed hydrogenation of a 24.8:75.2% *cis*/*trans* mixture of perfluoro-2-pentenes at 65 °C obtained by ^{19}F gas phase NMR.

Figure 1 shows the ^{19}F NMR spectra (339.8 MHz) taken during the hydrogenation of a 75.2:24.8% mixture of *trans* and *cis* perfluoro-2-pentenes (~119 μmol) in the presence of ~476 μmol of hydrogen, ~1 mol % palladium on alumina (relative to the olefin), and ~47 μmol of CF_4. The total pressure at 65 °C is ~3.1 atm. Three spectra are shown (a) at the start, (b) at an intermediate time, and (c) at the end of the reaction. The fluorine resonances of the *cis* and *trans* olefin isomers are labeled **C** and **T**, and those of the two HFCs are labeled **A** and **B**.[9] There are practically no byproducts (<1%), and the resonance of the CF_4 standard is invariant with time. The spectra were obtained by setting the spectrometer frequency in the middle of the spectrum, and a small flip angle (14°) was used for a uniform power distribution over the wide spectral width.[10] Under our conditions the CF_3 fluorines in the olefin reactants and in the HFC products have T_1 values of 32−50 ms, measured by the inversion recovery method, while the T_1 values of the CHF fluorines are longer by an order of magnitude.

The sensitivity can be greatly improved with a much greater flip angle (74°) and by setting the carrier frequency in the spectral region of the rapidly relaxing CF_3 fluorine resonances. The stacked spectra of Figure 1 were obtained in this manner. They show the partial time evolution of the resonances of the CF_3 fluorines of the perfluoroethyl groups of each reaction component. Each spectrum was the result of 16 transients yielding a signal-to-noise ratio greater than 1000 in 2.9 s. Because the resonances overlap to some extent (line widths of 50−60 Hz), the integral values, plotted in Figure 2 as relative concentrations, were obtained by an automated least-squares deconvolution that takes into account the drift of the unlocked field (~11 Hz/h).

The plot of Figure 2 reveals chemical information that would be laborious to obtain by conventional techniques. The data can be adequately fit by ordinary exponential functions indicating pseudo-first-order kinetics resulting presumably from the 4-fold molar excess of hydrogen that may be even greater on the catalyst surface.[11] The hydrogenation is clearly stereospecific since the rate of formation of each diastereomeric HFC product exactly mirrors the rate of decay of the corresponding olefin isomer. There is no isomerization of the olefins since the final ratio of the HFC products is exactly the ratio of the starting isomeric olefins. Most strikingly, however, the hydrogenation of the *trans* olefin (k_{trans}/k_{cis}) is 2.4 times faster than that of the *cis* olefin. This difference in hydrogenation reactivity of the isomeric fluoroolefins on the palladium surface, the opposite of that observed for hydrocarbon olefins (*cf.*, ref 7, p 447), is not the result of a lower concentration of the *cis* isomer. It is clearly an intrinsic property of the fluoroolefins in this reaction since it manifests itself also in an analogous experiment using a 1:1 mixture of *cis*/*trans* perfluoro-2-pentenes although the reactivity ratio in this experiment is somewhat different ($k_{trans}/k_{cis} = 3.5$).

The hydrogenation of a 74:26% mixture of *trans* and *cis* perfluoro-2-butenes under the same reaction conditions except for the temperature (60 °C) gave analogous results: complete stereoselectivity, no isomerization, excellent pseudo-first-order kinetics, and $k_{trans}/k_{cis} = 2.0$.

The reason for the slower hydrogenation of the *cis* isomers is unclear. However, we did study briefly the selective adsorption of the 2-butenes over both Pd/Al_2O_3 and pure palladium black. Sample preparation was the same except for an increased amount of freshly activated solids at the bottom of the ampules. With Pd/Al_2O_3, gas phase NMR revealed about 4% preferential adsorption of the *cis* isomer from the 74:26% mixture at 65 °C, whereas palladium black did not alter the *cis*/*trans* olefin ratio.

Our preliminary results demonstrate the utility of gas phase NMR as a new technique for heterogeneous catalysis. It appears to be particularly suited to follow the *relative* kinetics of volatile reaction components over a catalyst (when the reaction time scale and the diffusion limitations are compatible with the technique) and to study the competitive adsorption equilibria of volatile compounds over a variety of adsorbents.[12] The advantage of this technique over, for example, gas chromatography, is that NMR resonances not only carry information on the concentrations of reactants and products at any instant without sample extraction but also contain precise and easily decipherable structural information. Additionally, the short T_1 relaxation times in the gas phase under the conditions employed here allow rapid data acquisition, and the high automation and programmability of modern NMR spectrometers greatly facilitate repetitive spectral acquisitions and treatment of data in kinetic experiments

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(9) Gas phase ^{19}F chemical shifts (ppm) relative to $CFCl_3$ ($\delta(CF_4) = -63.5$ ppm). *Trans*: C1, −69.8; C2 and C3, −158.2; C4, −121.1; C5, −85.0. *Cis*: C1, −66.0; C2, −139.0; C3, −142.4; C4, −118.3; C5, −84.1 (65 °C). HFC **B**: C1, −78.2; C2 and C3, −219.1 and −219.7; C4, AB with A at −123.1 and B at −140.7 ($^2J_{FF} \approx 290$ Hz); C5, −83.7. HFC **A**: C1, −78.2; C2 and C3, −208.9 and −212.5; C4, overlapping with C4 of HFC **B**; C5, −83.2 (65 °C).

(10) Acquisition time = 57 ms, pulse repetition rate = 157 ms, number of transients = 16, total time for one spectrum = 2.5 s.

(11) The initial points obtained when the temperature has not yet equilibrated are discarded. The exponentials do not extrapolate exactly to the starting concentrations at time zero (see starting olefin concentrations on the ordinate axis) presumably because of insufficient diffusional mobility.

(12) We are aware of only one study that uses gas phase NMR to study the equilibration of two gases over a solid: Ernst, H.; Kärger, J. *Z. Phys. Chem. (Leipzig)* **1987**, *268*, 321.