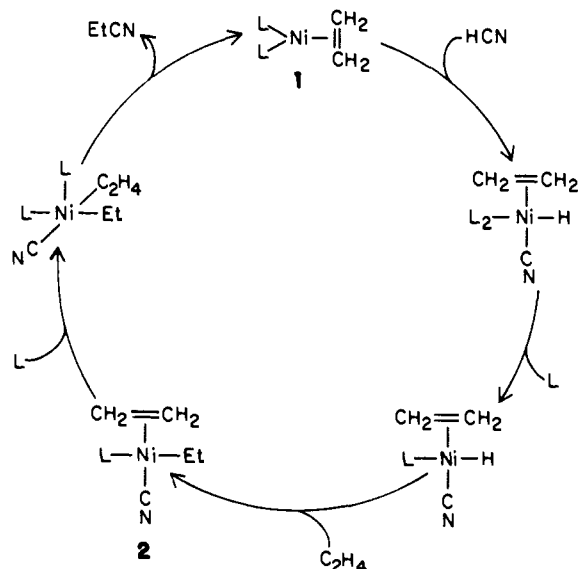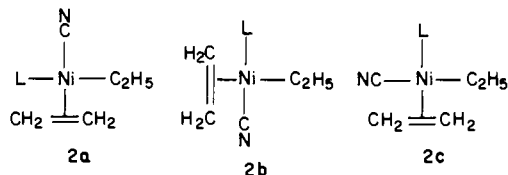**Scheme I**

employed as catalyst, we were surprised to find an apparent second-order rate dependence on the initial concentration of **1**,[2] with a large negative entropy of activation [at −40 °C, $k = 7.6 \pm 0.8 \times 10^{-4}$ L/(mol s); $\Delta H^{\ddagger} = 8.9 \pm 0.9$ kcal/mol; $\Delta S^{\ddagger} = -34 \pm 4$ eu].[3] The reaction rate is independent of ethylene and hydrogen cyanide concentrations.

Examination of the system by ^{31}P NMR spectroscopy[4] revealed that, upon addition of HCN in the presence of excess ethylene at −40 °C, the resonance of **1** at 141.4 ppm is quantitatively replaced by four new singlets at 129.8, 118.1, 117.7, and 116.9 ppm with areas in a relative ratio of 1.00:0.14:0.80:0.06. The signal at 129.8 ppm is assigned to free $(o\text{-tolyl-O})_3$P. These signals persist until HCN and/or ethylene are consumed. Reexamination of the proton spectrum reveals a multiplet at δ 0.61 assigned to a Ni–C_2H_5 species,[1] a singlet at δ 2.03 assigned to coordinated ethylene, and a broad singlet at δ 2.09 assigned to the methyls of $(o\text{-tolyl-O})_3$P, both coordinated and uncoordinated. The ^{13}C NMR spectrum at −50 °C using ^{13}C^{12}CH$_4$-enriched ethylene[5] shows signals assigned to a Ni–C_2H_5 unit at 14.1 and 11.7 ppm, the latter a doublet with $J_{CP} = 35$ Hz, indicating coupling to one phosphorus in a trans position,[5] as well as a signal for coordinated ethylene at 58.9 ppm.

On the basis of these data, the intermediate species are assigned the isomeric structures of **2a–c** with **2a** being the predominant

isomer based on the carbon–phosphorus coupling constant.[5] Whether all isomers participate in catalysis is unclear, but

equilibration among the isomers appears to be faster than the catalytic reaction.

The apparent second-order rate dependence on **1** results from the production of **2** and free ligand which must recombine in the final slow step to produce propionitrile and **1**. Indeed, we have confirmed the second-order rate law,

$$d[\text{EtCN}]/dt = k[\mathbf{2}][\text{L}]$$

where k is the same second-order rate constant described above; the rate law is obeyed over at least tenfold concentration changes in each component. We propose the mechanism shown in Scheme I.

The rate dependence on the ligand concentration and the large negative entropy of activation suggest that a five-coordinate nickel species is formed prior to reductive elimination of propionitrile. This proposal is consistent with earlier observations on reductive elimination of organonitrile[6] and supports the recent theoretical analysis of Tatsumi et al.;[7] they suggest that reductive elimination from five-coordinate nickel species will usually be preferred over three- or four-coordinate counterparts primarily because of the stability of the nickel fragment produced. In our case, the generated fragment is an isolable complex whose stability must contribute greatly to the driving force of the reaction.

In light of proposals that oligomerization and polymerization of ethylene on nickel catalysts proceed through a (C_2H_4)Ni–C_2H_5-containing intermediate,[8] it is interesting to note that no butenes or hexenes or hydrocyanation products thereof are detected under our reaction conditions.

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Useful Approach for Determination of the Structure of Organosulfur Compounds: Sulfur-33 High-Resolution FT-NMR

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While the NMR spectra of many different nuclei have proved useful in organic structure determination, sulfur-33 NMR spectroscopy has been conspicuously absent. The vast importance of organosulfur chemistry demands an examination of this untapped tool. We show here that the combination of sulfur-33 line-width and chemical-shift data is a powerful diagnostic indicator. Compounds of the type R(SO$_2$)R' are usually amenable to ^{33}S NMR studies, which can provide relatively routine, unambiguous structural information not available from ^{13}C and ^{1}H NMR experiments. Compounds of the type RSR, RS(O)R, and RS(O)OR generally have line widths that are too broad (1000–5000 Hz) for routine ^{33}S NMR experiments. In the course of studies designed to explore the chemistry of acyl sulfones,[1] the carbomethoxy

(2) Measurements were obtained on a Nicolet NT-360 MHz NMR spectrometer at 360.961 MHz. T_1 measurements were obtained for all species from −50 to −10 °C and pulse delays set accordingly. Samples were prepared in a Vacuum Atmosphere drybox in toluene-d_8 with concentration of **1** ranging from 0.01 to 0.10 M and concentrations of HCN and C_2H_4 generally about 0.26 and 0.20 M, respectively. CH_2Cl_2 (0.50 M) was used as an internal standard for proton spectra.

(3) Second-order rate constants were obtained from **1** (0.05 M in toluene-d_8) at −10, −20, −30, −40, and −50 °C. Activation parameters were estimated by nonlinear least-squares analysis of the experimental data.

(4) ^{31}P NMR spectra were obtained on a Nicolet 360-MHz NMR spectrometer at 146.14 MHz or on a Nicolet 300-MHz instrument at 121.68 MHz. T_1 measurements were obtained at ambient temperature and pulse delays set accordingly. Samples were prepared as in ref 2. Chemical shifts are referenced to external phosphoric acid.

(5) ^{13}C NMR spectra were those described in ref 1 and were obtained both with ^{13}C^{12}CH$_4$ and ^{13}C$_2$H$_4$ at −50 °C on the Nicolet 360-MHz instrument at 90.80 MHz. Chemical shifts are referenced to tetramethylsilane.

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Table I

compd	chem shift,^{a,b} ppm				line width, Hz			
CS$_2$	−371 (0.0) (0.0)	(0.0)	(0.0)		284			340
CH$_3$SCH$_3$ (NPh)	−84 (287)				274			
CH$_3$CH=CHSO$_2$Ph	−61 (310)		(305)		50			115
Ph$_2$SO$_2$	−60 (311) (312)	(306^e)	(308)		48	120	130^e	161
(O SO$_2$ ring)	−56 (315) (315)				20	100		
CH$_3$—C$_6$H$_4$—SO$_2$CH$_3$ (SCO$_2$CH$_3$)	−57^{d,g} (314)				283^d			
CH$_3$—C$_6$H$_4$—SOCO$_2$CH$_3$	h							
(PhSO$_2$)$_2$CH$_2$	−56 (315)				586^k			
CH$_3$—C$_6$H$_4$—SO$_2$CH$_3$	−56 (315)				48			
PhSO$_2$CH$_3$	−55 (316)	(307^e)			35		120^e	
CH$_3$SO$_2$CH$_2$CO$_2$CH$_3$	−50 (321)				78			
(CH$_3$)$_2$SO$_2$	−49^{d,g} (322) (320)	(322^e)	(315)		6.8^{d,g}	50	50^e	46
(CH$_3$)$_2$SO$_2$, ^{1}H coupled	−49^{d,g} (322)				14.6^{d,g}			
H$_2$C=CHCH$_2$SO$_2$Ph	−48 (323)				50			
PhCH$_2$S(=O)$_2$CO$_2$CH$_3$	−44 (327)				240^g			
Na$_2$SO$_4$	−43^f (328)	(329^f)			6.5^f			
CH$_3$SCH$_2$SO$_2$Ph	−41 (330)				39			
(ring SO$_2$)	−9.0 (362) (361)	(360^e)			14	50	50^e	
(ring SO$_2$)	0.0 (371) (370)	(369^e)	(368)		9.8	50	50^e	69
CH$_3$—C$_6$H$_4$—SO$_2$NH(NH$_2$)	not observable				not observable			
CH$_3$—C$_6$H$_4$—SO$_2$N(CH$_3$)(NO)	not observable				not observable			
CH$_3$—C$_6$H$_4$—SO$_2$CN	not observable				not observable^j			
(CH$_3$)$_2$SO	−138 +/− 20^c neat (233)	325			2500^c neat			5520
(ring S)	−151 +/− 6^c in CS$_2$ (220)				650^c in CS$_2$			

^{a} Chemical shifts are all referenced to that of sulfolane = 0 ppm. Chemical shift values with CS$_2$ as the zero reference are given in parentheses. Solvent is deuterochloroform unless otherwise noted. ^{b} The chemical shift values in column 1 are the present work. Columns 2, 3, and 4 are from ref 4, 5, and 11, respectively, and similarly for the line width values. ^{c} Values taken from ref 6. ^{d} Acetone-d_6 used as a solvent. ^{e} Me$_2$SO used as a solvent. ^{f} D$_2$O used as a solvent. ^{g} DMF used as a solvent. ^{h} This possible structure was not observed. ^{i} The surprisingly large line width may be due to exchange between the sulfone and the sulfinate. See eq a and ref 3. ^{j} It is conceivable that an equilibrium of the type represented in eq a is also responsible for the extraordinary line width for this compound. ^{k} We have at this time no explanation for this very broad line, but it may be related to the presence of two identical sulfones in a 1,3-relationship.

sulfone 1^2 was presumed to have been prepared; however, the chemistry of the species seemed better in accord with structure 2.^{3} While infrared spectroscopy and proton and carbon-13 NMR spectroscopy seemed to support structure 1, they were not definitive. On the other hand, because of the difference in electronic symmetry at the sulfur nucleus in 1 and 2 sulfur-33 NMR

RS(=O)$_2$CO$_2$CH$_3$ RS(=O)OCO$_2$CH$_3$ (a)
     1   **2**
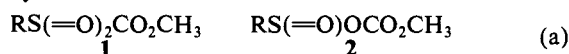
spectroscopy should offer an unambiguous answer to this question. We wish to report the first use of this technique for structure determination.

To date there are very few reports of high-resolution sulfur-33 NMR studies.$^{4-9}$ and the narrowest lines reported in the literature

for organosulfur compounds are 50 Hz or greater.^{4,5,11} We report here lines as narrow as 6 Hz. The values for $v_{1/2}$ and T_1 are related to the electric field gradient at the nucleus and to the molecular motion of the molecule by the relation^5

$$\pi v_{1/2} = 1/T_1 = R_1 =$$

$$\frac{3}{40}\left[\frac{2I+3}{I^2(I+1)}\right](1 + \eta^2/3)(eqeQ/\hbar)^2\tau_c \quad (1)$$

If we make the reasonable approximation^{10} that $\eta = 0$ and use

(2) Related carboalkoxy sulfones have been reported but this structural ambiguity was not considered. See: Ferdinand, G.; Schank, K. *Synthesis* **1976**, 408. Barton, D. H. R.; Manly, D. P.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1568. Olijnsma, T.; Engberts, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 897. Senning, A.; Sorenson, O. N.; Jacobsen, C. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 734.

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the fact that for sulfur-33 $I = \frac{3}{2}$, then we obtain

$$\pi v_{\frac{1}{2}} = R_1 = 1/T_1 = 0.1(eqeQ/\hbar)^2\tau_c \qquad (2)$$

where *eq* is the electric field gradient at the sulfur nucleus and *eQ*, a fixed constant, is the nuclear quadrupole moment. τ_c is the molecular correlation time and is a measure of how rapidly the molecule moves from one orientation to an appreciably different one in its environment. For nonviscous liquids at room temperature τ_c is usually about 10^{-12} s. The value of the sulfur-33 quadrupole coupling constant $(e^2qQ/\hbar)$ ranges from about 2 Hz to about 5 MHz. Thus for highly symmetric environments such as exist in sulfones, we expect relaxation times of 100-900 ms or line widths of a few hertz. For highly unsymmetric environments we expect T_1 values of 100 μs or less and line widths of several kilohertz or more (see ref 10, Chapter 4 for more details).

Since τ_c is temperature dependent $(\tau_c = \tau_o \exp(v/(RT)))$, we can obtain sharper sulfur-33 resonance lines by working at elevated temperatures and, wherever possible, by using low-viscosity solvents. For example, Me$_2$SO is a poor solvent because it has a high viscosity, which leads to broader lines.

In the NMR measurements presented here we have used relatively high temperatures (30-45 °C) and low-viscosity solvents. The spectra were obtained at 15.339 MHz on a JEOL FX-200 spectrometer using 15-mm-diameter sample tubes or at 20.710 MHz on an IBM-WP-270 spectrometer using 10-mm-diameter sample tubes. In most cases, for the 10-mm sample tubes, about 1 g of sample was dissolved in about 1.5 mL of solvent. One-half hour or less of signal averaging was usually enough to give a signal-to-noise ratio, S/N, of 20/1 or better. In all cases proton decoupling was used to remove residual, long-range proton-sulfur spin-spin coupling.

The chemical-shift and line-width values that we obtained are summarized in Table I. For comparison, we have also listed in Table I the chemical-shift and line-width values obtained in ref 4 and 5. The agreement between the chemical shift values is reasonably good, especially considering the rather broad lines observed in the two earlier references.

We have recorded sulfur-33 spectra for (CH$_3$)$_2$SO$_2$ both with and without proton coupling. The proton-decoupled spectrum at 40 °C has a line width of 6.8 Hz. The proton-coupled sulfur-33 spectrum has a line width of about 15 Hz. Since the protons are all equivalent, one might expect the sulfur-33 spectrum to be a heptet with a splitting of J_{S-H} Hz between each of the lines in the multiplet. Due to the width of the individual lines the fine structure is not observed. Based on the width of the observed line at half-height one expects a value of J_{S-H} of about 3 Hz for dimethyl sulfone.

On the basis of the present work and that in the literature[3-6] it is clear that four-coordinate sulfur, such as in sulfones and sulfonic acid derivatives, has *both* line widths and chemical shifts that are quite different from those in sulfoxides, sulfides, and thiophenes. Consequently it is quite clear that the structure of **1** must be that depicted and not **2**.

Registry No. CS$_2$, 75-15-0; PhN=S(O)(CH$_3$)$_2$, 56157-97-2; CH$_3$CH=CHS(O)$_2$Ph, 28975-80-6; Ph$_2$S(O)$_2$, 127-63-9; CH$_2$CH$_2$O-CH$_2$CH$_2$S(O)$_2$, 107-61-9; CH$_3$-*p*-C$_6$H$_4$S(O)$_2$CO$_2$CH$_3$, 60279-10-9; CH$_3$-*p*-C$_6$H$_4$S(O)OCO$_2$CH$_3$, 93714-76-2; (PhS(O)$_2$)$_2$CH$_2$, 3406-02-8; CH$_3$-*p*-C$_6$H$_4$S(O)$_2$CH$_3$, 3185-99-7; PhS(O)$_2$CH$_3$, 3112-85-4; CH$_3$S-(O)$_2$CH$_2$CO$_2$CH$_3$, 62020-09-1; (CH$_3$)$_2$S(O)$_2$, 67-71-0; H$_2$C=CHCH$_2$S(O)$_2$Ph, 16212-05-8; PhCH$_2$S(O)$_2$CO$_2$CH$_3$, 93714-77-3; Na$_2$-SO$_4$, 7757-82-6; CH$_3$SCH$_2$S(O)$_2$Ph, 59431-14-0; CH$_2$CH=CHCH$_2$-S(O)$_2$, 77-79-2; CH$_2$CH$_2$CH$_2$CH$_2$S(O)$_2$, 126-33-0; CH$_3$-*p*-C$_6$H$_4$S-(O)$_2$NH(NH$_2$), 1576-35-8; CH$_3$-*p*-C$_6$H$_4$S(O)$_2$N(CH$_3$)(NO), 80-11-5; CH$_3$-*p*-C$_6$H$_4$S(O)$_2$CN, 19158-51-1; (CH$_3$)$_2$SO, 67-68-5; CH=CHC-H=CHS, 110-02-1; ^{33}S, 14257-58-0.

Raman Spectroscopic Study of Acetylene on Supported Rhodium Catalysts

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There exists a relatively large body of experimental observation concerning the interaction of small hydrocarbon molecules with group 8 metals.[1,2] Synthetic chemists have amassed a wealth of data concerning the distribution of reaction products for hydrogenation reactions on these metals which indicate that cis addition to unsaturated adsorbates is predominant.[3,4] This information is to be contrasted with the microscopic information obtained by using conventional surface science experimental techniques which have detected surface intermediates not having obvious preference for cis vs. trans products.[1] Surface hydrocarbon chemistry has been probed by a wide variety of methods including electron energy loss spectroscopy (EELS),[5] low-energy electron diffraction (LEED),[6] secondary ion mass spectrometry (SIMS),[7] ultraviolet photoelectron spectroscopy (UPS),[8] and near edge X-ray fine structure spectroscopy (NEXAFS).[9] All of these experimental techniques require ultrahigh vacuum conditions and consequently are not necessarily sensitive to the species of importance under catalytically relevant conditions. Surface-sensitive probes that can operate under higher pressures and coverages are clearly desirable. Optical spectroscopies, such as Raman spectroscopy, provide such a probe since photons rather than charged particles interact with the surface, and they are not scattered efficiently by the gas phase. Surface-enhanced Raman spectra of organic adsorbates on catalytically important group 8 metals have recently been described.[10] This paper reports enhanced Raman spectra of acetylene on a supported rhodium catalyst and the identification of $\sigma_2\pi$-C$_2$H$_2$(ads) on this surface under conditions in which it has

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