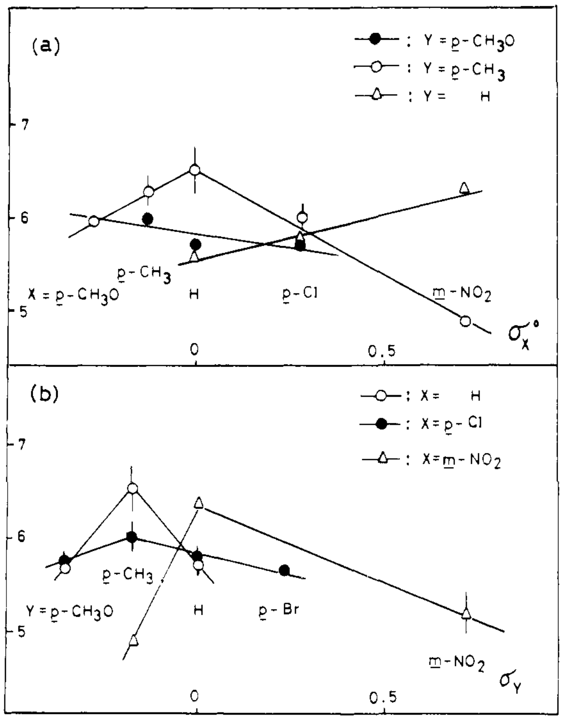

Figure 1. Variation of carbon-14 kinetic isotope effects in the Menschutkin-type reaction: (a) Y fixed, X varied; (b) X fixed, Y varied.

Table I. Rate Constants and Carbon-14 Kinetic Isotope Effects in the Menschutkin-Type Reaction of Benzyl Benzenesulfonates and *N,N*-Dimethylanilines[a]

Y	X	$10^4 k_2$, L mol^{-1} s^{-1}	k^{12}/k^{14}
p-CH$_3$O	*p*-CH$_3$	8.72 ± 0.21	1.148 ± 0.002
	H	17.1 ± 0.1	1.140 ± 0.003
	p-Cl	62.6 ± 0.8	1.142 ± 0.002
p-CH$_3$	*p*-CH$_3$O	2.36 ± 0.07	1.147 ± 0.002
	p-CH$_3$	3.84 ± 0.06	1.156 ± 0.005
	H	7.82 ± 0.01	1.162 ± 0.008
	p-Cl	27.2 ± 0.7	1.149 ± 0.004
	m-NO$_2$	252 ± 4	1.119 ± 0.003
H	H	3.41 ± 0.03	1.135 ± 0.003
	p-Cl	12.9 ± 0.1	1.143 ± 0.003
	m-NO$_2$	101 ± 1	1.158 ± 0.001
p-Br	*p*-Cl	3.88 ± 0.04	1.139 ± 0.002
m-NO$_2$	*m*-NO$_2$	8.60 ± 0.16	1.127 ± 0.006

[a] In acetone at 45 °C. Concentration: 0.007–0.015 L mol^{-1} in ester and 0.015–0.060 L mol^{-1} in nuclephile.

Thornton,[9] Thornton,[10] and Harris and Kurz,[11] a transition-state structure in an S$_N$2 reaction becomes more reactant-like (product-like) when the nucleophile becomes more (less) nucleophilic or the leaving group becomes a better (poorer) one. Judging from its maximum isotope effect (Figure 1b, X = H curve), the transition-state structure must be symmetric in terms of force constants of the two reacting bonds in the case of Y = *p*-CH$_3$ and X = H. Then, when the substituent Y is changed to a more electron-withdrawing one, H, the transition state shifts to be more product-like, and the unsymmetric transition state results in a smaller isotope effect. However, by then changing the substituent X to be more electron withdrawing (Figure 1b, changing from X = Y = H to X = *m*-NO$_2$, Y = H), the transition state recovers its symmetry and gives a larger isotope effect. Similarly, the monotonous trends in Figure 1a can be reasonably explained.

Another fact which is apparent from Figure 1 is that the maximum position shifts to a much smaller extent in Figure 1b than in 1a. In other words, substituent Y has a larger effect on the magnitude of the isotope effect than substituent X has. This may be a characteristic of a typical S$_N$2 reaction in which the bond formation is much more important than the bond breaking as a driving force of the reaction.

In conclusion, these kinetic isotope-effect results provide clear-cut evidence for the validity of the theory concerning the variation of the transition-state structure with substituent. Because of the advantageous characteristics of this reaction system, further investigations are underway.

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$$\log (A_\infty - A_x x) = k^{14}/k^{12} \log (1 - x) + \log A_\infty \qquad (3)$$

(8) Rate study on this system indicated that the best correlations are obtained by use of σ^0 and σ as the substituent constants of X and Y, respectively. Tsuno, Y.; Fujio, M.; Yoh, S. D.; Sawada, M.: Yukawa, Y. Abstract of the 25th Conference on Organic Reaction Mechanism, Tokyo, 1974; the Chemical Society of Japan: Tokyo, 1974; pp 199–202.
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Direct Tungsten-183 Nuclear Magnetic Resonance: a Powerful New Structural Tool for Heteropoly- and Isopolytungstate Chemistry

Sir:

Heteropoly and isopoly electrolytes constitute a distinct fundamental category of compounds of very sizable potential variety and importance.[1-3] However, only a relatively modest number of structural types has been elucidated.[2,3] Generally speaking, the poly*tungstates* are among the most diverse, stable, and readily purified of these compounds. This paper reports the first successful direct observation of ^{183}W NMR spectra for heteropoly- and isopolytungstates and, using several compounds, demonstrates that such spectra can be readily obtained (e.g., using a Bruker WH-90 FT spectrometer), are clear-cut, and provide a very powerful new tool for elucidation of structures in solution, with respect both to bonding and to relative atomic positions.

^{183}W, with spin $1/2$ and at 14.27% abundance, is the only NMR-active isotope in natural W. Its sensitivity is 7.0×10^{-5} that of the proton. It was recently observed directly in simple WO_4^{-2} ion, WF_6, and WCl_6 by Banck and Schwenk,[4] who relied on the quadriga transform technique, which yielded broader lines than those reported herein. ^{183}W, again in simple compounds, has also been directly observed by Gansow,[5] who used a 180-MHz FT instrument. Various ^{19}F and ^{183}W NMR measurements on WF_6 have shown the W–F coupling constant to be small, the reported values[4-6] ranging from 41 to 48 Hz.

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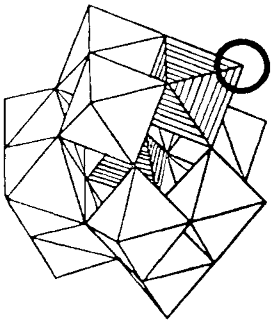

Figure 1. The structure of $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ and of $[X^{n+}W_{11}O_{39}]^{(12-n)-}$. Each vertex of a polyhedron locates the center of a close-packed oxygen atom. The heteroatom, X, is within the central hatched tetrahedron. In the 12-tungsto complexes, every octahedron contains a W atom. In the 11-tungsto complexes one W (e.g., from the hatched octahedron) and one of its O atoms (the unshared, circled one) have presumably been removed. The $[X_2^{5+}W_{18}O_{62}]^{6-}$ structure may be formed by plucking from each of two 12-tungsto complexes, the bottom three W octahedra shown in the figure. The two 9-tungsto "half-units" so formed are then joined by inverting one of them and sharing the six oxygen sites on the bottom of the uninverted complex with the corresponding six sites on the top of the inverted complex.

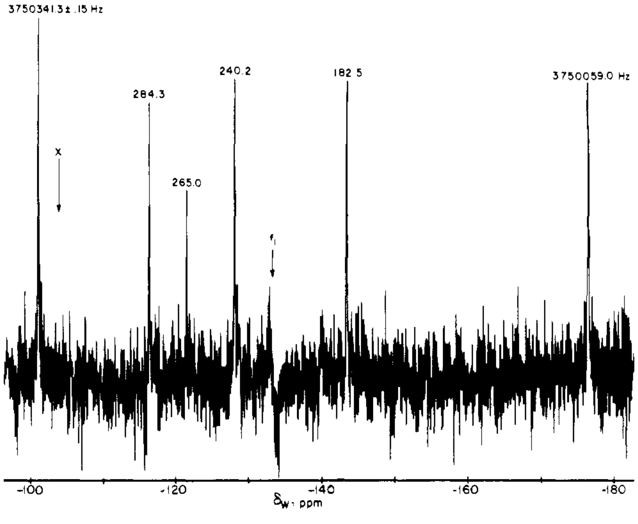

Figure 2. ^{183}W NMR spectrum of $[SiW_{11}O_{39}]^{8-}$. Discussion appears in the text. δ_W values are relative to Na_2WO_4 at pD 9.1. X marks the position of the single peak of $[SiW_{12}O_{40}]^{4-}$.

The spectra reported herein are remarkably sharp, with line widths at half-height averaging well under 1 Hz. We have chosen the ^{183}W resonance in saturated D_2O solution of Na_2WO_4 at 28 °C and pD 9.1 as the reference in terms of which chemical shifts are reported as δ values.[7] That ^{183}W frequency is 3 750 719.9 Hz in a field at which the protons of TSP[8] resonate at 90 023 349.9 ± 0.3 Hz using a D_2O lock. All of the spectra were recorded at 28 °C in the pulse mode using 10-mm spinning sample tubes in a Bruker WH-90 spectrometer operating at 90.02 MHz and locked on D_2O.

In the well-known Keggin structure[2] complexes, $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (see Figure 1), the 12 W positions are identical. The free acids of such anions wherein X = P^{5+}, Si^{4+}, B^{3+}, and H_2^{2+} were measured at pD 1.5. Each spectrum consisted of a single sharp peak ($\Delta\nu_{1/2} < 1$ Hz). Spectra of the Si complex at six pD values between 1.5 and 5.2 showed no change with acidity, indicating no change with pH within the pH stability ranges for the 12-tungsto complexes. The chemical shifts of the ^{183}W in the respective compounds were remarkably sensitive to the identity of the heteroatom, being δ −130.39 ± 0.05 ppm for $[BW_{12}O_{40}]^{5-}$, δ −111.26 ± 0.05 ppm for metatungstate, $[H_2W_{12}O_{40}]^{6-}$, δ −103.83 ± 0.05 ppm for $[SiW_{12}O_{40}]^{4-}$, and a narrow doublet centered at δ −98.83 ± 0.05 ppm for $[PW_{12}O_{40}]^{3-}$. Depending upon the number of pulses used (16-37 K), the signal to noise ratios for these spectra were in the range (10-17):1 without exponential multiplication.

The small size of the one-bond W-F coupling constant cited above indicates that the two-bond W-O-X couplings are probably very small in the heteropoly tungstates. As expected, no coupling was observed for the metatungstate, the B, or the Si complexes. ^{31}P, at 100% abundance, is an excellent coupler, however. The clarity of these spectra is illustrated by the splitting of the ^{183}W peak in $[PW_{12}O_{40}]^{3-}$ into a base-line-resolved doublet, showing a W-O-P coupling constant of 1.05 ± 0.15 Hz with average line widths of ~0.2 Hz at half-height. We believe that this represents the minimum line width imposed by our instrument and not necessarily the actual natural line width for the compound.

Many Keggin structure 12-heteropoly complexes react when the pH values of their solutions are raised in a controlled way, to yield 11-heteropoly species, formulated as $[X^{n+}W_{11}O_{39}]^{(12-n)-}$ (see Figure 1). Indirect evidence, such as their reactions to form dihetero-11-heteropoly derivatives,[2,9,10] has led to the conclusion that the structure of the 11-heteropoly species is probably identical with that of a Keggin unit with one octahedral W (and its unshared oxygen) plucked out. Direct evidence on this point is more difficult since the complexes crystallize with the positions of the "missing" W atoms disordered, thereby thwarting clear X-ray interpretation; and the condition in solution is still more problematical.

The sodium salt of $[SiW_{11}O_{39}]^{8-}$ was prepared. That complex, in 0.9 M solution at pD 7 and 8.4, gave the spectrum shown in Figure 2, consisting of six very clearly separated peaks. Examination of Figure 1 will show that the widely accepted structure of $[SiW_{11}O_{39}]^{8-}$ has five pairs of structurally identical W atoms and one unique W atom. The peak areas are roughly in the ratio 2:2:1:2:2:2. The precise experimental area ratios are 2.0:1.6:1.0:2.0:2.0:2.0. The slightly smaller size of the second peak is attributable to a different relaxation time.

This experiment is not only important in substantiating the current structural hypothesis, but it demonstrates the great sensitivity of the ^{183}W chemical shifts among different, but structurally very similar, sites.

The $[X_2^{5+}W_{18}O_{62}]^{6-}$ complexes are of established structures and isomerisms.[11,10] The structures are closely related to the Keggin structure (Figure 1), the complexes being formed by joining two "half-units", each of which is made by removing the bottom three W octahedra from the structure shown in Figure 1.[10] The ^{183}W spectrum of the most stable isomer of $[P_2W_{18}O_{62}]^{6-}$ (Pope's "α-isomer", Wu's[12] "B-isomer") was measured at pD 1.5. The structure contains 12 equivalent W atoms around its "belt" and six equivalent W atoms capping its "ends".[10] The ^{183}W spectrum contained just two narrow base-line-resolved doublets, well separated from each other and from the position of the $[PW_{12}O_{40}]^{3-}$ resonance. The area ratio of one doublet to the other was 2.0:1.0. The larger one was centered at δ −170.14 ± 0.05 ppm with $^2J_{W-O-P}$ = 1.50 ± 0.15 Hz, and the smaller doublet was centered at δ −124.87 ± 0.05 ppm with $^2J_{W-O-P}$ = 1.35 ± 0.15 Hz. Although the ±0.15-Hz estimates of individual error ranges for the absolute values of these J values make them appear close to overlap, the assignment of the *relative* sizes of the J values is more accurate.

The PO_4 groups in these complexes are probably the smallest heteroatom tetrahedra in this class of compounds. That the central PO_4 in $[PW_{12}O_{40}]^{3-}$ does not "rattle", but is firmly fixed at the center of the complex, is shown by the small temperature factors, for the atoms in that tetrahedron, found by single-crystal X-ray structure determinations.[13] However, the O-W distance (from tetrahedron to W) is longer than for other

Keggin structures.[14] When a $[PO_4W_9O_{30}]^{9-}$ "half-unit" is made from a Keggin structure by plucking off three WO_6 octahedra[10] (caption, Figure 1), the PO_4 tetrahedron is free to move a little closer to the remaining W atoms. Thus in $[P_2W_{18}O_{62}]^{6-}$, formed by joining two of the 9-tungsto half-units, the P-O-W distances remain slightly shorter than in $[PW_{12}O_{40}]^{3-}$. According to recent very accurate crystal structures, the average P-O-W distance[14] in the PW_{12} complex is 3.97 Å; the average P-O-W distance[15] for the six "capping" W atoms in the P_2W_{18} complex is 3.94 Å; and the average P-O-W distance[15] from each P atom to the six "belt" W atoms closest to it is 3.90 Å. These averages are more accurate than the individual distances.

The fact that the $^{2}J_{P\text{-}O\text{-}W}$ values are larger for the $[P_2W_{18}O_{62}]^{6-}$ than for the $[PW_{12}O_{40}]^{3-}$ is consistent with the slightly shorter P-O-W distances in the former complex. The sharpness and simplicity (owing to $I = 1/2$) of the spectra which yield the respective J values, as well as the differences in the δ values for the structurally very similar W atoms in these two complexes, emphasize the clarity and potential sensitivity of ^{183}W NMR for elucidating subtle structural differences.

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(16) From a portion of the Georgetown University Ph.D. Dissertation of Rafael Acerete, who is on leave from the Department of Chemistry, School of Pharmacy, University of Valencia, Spain.

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Optical Activity as a Mixed Parity Phenomenon

Sir:

It has been suggested that natural optical activity provides a subtle example of broken symmetry, originating in the loss of the inversion symmetry of the medium as a whole.[1] The argument rests on the requirement that an ideal stationary state (one that has an infinite lifetime and is independent of the previous history of the system) must be an eigenstate of the parity operator since it must have the full symmetry of the complete Hamiltonian of the system. Consequently, a molecule in an ideal stationary state cannot show optical activity because the corresponding rotational strength vanishes. This is because the rotational strength involves the scalar product of an electric dipole and a magnetic dipole transition moment between the same initial and final molecular states, and the electric and magnetic dipole moment operators have opposite parity. A gedanken experiment was proposed in which, on taking a resolved enantiomer of a small optically active molecule in the gas phase and doing everything possible to eliminate intermolecular interactions and increase the resolution in energy, the optical activity might disappear abruptly, signaling the observation of transitions between ideal stationary states.[2] While it may be necessary to abandon the molecular structure hypothesis in order to savor fully the implications of such a hypothetical experiment,[1,2] it is worth pointing out for the benefit of the perplexed stereochemist that, by utilizing the concept of mixed parity quantum states that are quasi-stationary in the sense that they are only stationary on the time scale of our measurements, the molecular structure hypothesis allows an individual, resolvable, chiral molecule to show optical activity.

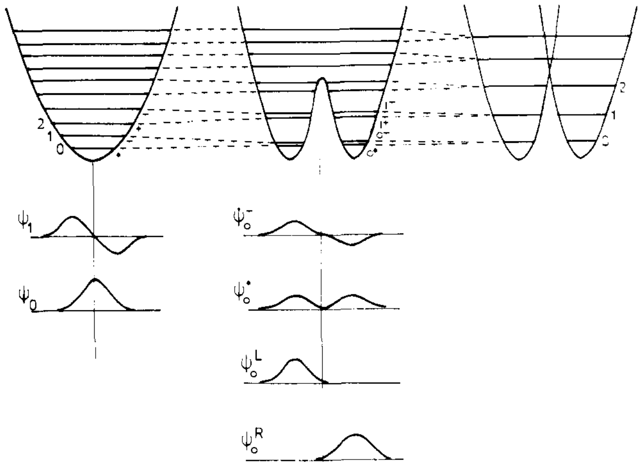

Figure 1. The vibrational states of a molecule that can invert between two equivalent configurations. ψ_0^+ and ψ_0^- are two definite parity states for which there is complete uncertainty, and ψ_0^L and ψ_0^R are two mixed parity states for which there is complete certainty, about whether the molecule is in the left or right well.

Odd Parity Observables and Mixed Parity States. Although eigenstates of opposite parity can never be exactly degenerate since they can never constitute a basis set spanning a degenerate irreducible representation, nonetheless they can often be sufficiently close in energy so as not to be resolvable in particular experiments, in which case the system appears to be in a state of mixed parity. Measurements on a system in a state of definite parity can reveal only observables with even parity, examples being electric charge, magnetic dipole moment, electric quadrupole moment, etc., whereas measurements on a system in a state of mixed parity can reveal, in addition, observables with odd parity, examples being linear momentum, electric dipole moment, etc.[3] A famous example of a system that can be observed in states of mixed parity is the hydrogen atom: although the states with $n = 2, l = 0$ and $n = 2, l = 1$ are not exactly degenerate because of a small relativistic splitting, in all but the weakest electric fields[1] the first excited state of the hydrogen atom shows a first-order Stark effect, one interpretation of which is that the first excited state possesses a permanent electric dipole moment.[4]

The optical rotatory parameter is a pseudoscalar[5] and so has odd parity. It is easy to see that the optical rotation experiment conserves parity because, if one inverts the entire experiment (the light beam plus the active medium), the resulting experiment is also realized in nature.[6] Consequently, resolved chiral molecules exist in quantum states of mixed parity.

Mixed Parity States of a Chiral Molecule. The origin of these mixed parity states can be appreciated by considering

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