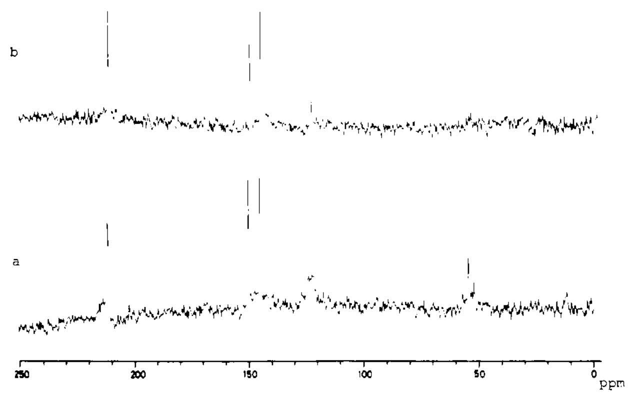

Figure 2. ^{15}N NMR spectra of 95% ^{15}N-enriched G*-G-C-Up in aqueous solution (70 mM in 0.1 M NaCl): (a) without proton decoupling (accumulated 100 times by 45° pulse with 10-s repetition interevals); (b) with selective proton decoupling (irradiated at 10.6 ppm in proton resonance frequencies and accumulated 100 times by 45° pulse with 10-s repetition intervals).

360-MHz ^1H NMR spectra of G-G-C-Up in H_2O (strand concentration is 44 mM in 0.1 M NaCl solution) were taken by Redfield pulse sequences[11] and are shown in Figure 1. At 3 °C three resonances are observed at 13.6, 12.0, and 10.6 ppm downfield from the DSS reference. Chemical shifts were initially read relative to the G-C^8H proton resonance and were converted to those of DSS. Raising the temperature to 10 °C causes the sharpest signal to 13.6 ppm to be still observed while the other two signals almost disappear. Therefore, this sharpest signal must be the resonance of G-N^1H of the G·C base pair, which is more stable than the G·U pair and, moreover, is in an internal position of the duplex. The resonance position (13.6 ppm) also supports the assignment since G-N^1H of G·C pair is usually observed in the 12–14 ppm region. The other two signals, which disappear simultaneously upon increasing temperature, must be G-N^1H and U-N^3H of the G·U pair. These assignments were supported by the appearance of an NOE at the 12.0 ppm peak under weak single-frequency preirradiation in 10.6 ppm. The observation pulse was applied with 1-ms delay after preirradiation for 0.1 s.[6]

The G-N^1H of the G·U pair was unambiguously assigned by measuring ^1H NMR spectra of G*-G-C-Up (Figure 1d). The 5′-terminal guanosine residue contains ^{15}N, and the imino proton should be coupled with the ^{15}N. When the spectra of G-G-C-Up and G*-G-C-Up are compared, the imino proton resonance of G*-G-C-Up in the highest field shows a splitting (J_{NH} = 90 Hz) and, therefore, must be the G*-N^1H of the G·U base pair. The relative resonance intensities of the G·U imino proton signals of G*-G-C-Up are larger than those of G-G-C-Up because of higher melting temperature due to higher concentration (70 mM) of the tetramer. In proton-coupled 36-MHz ^{15}N spectra at 5 °C, five peaks are observed at 52, 122, 144, 148, and 210 ppm downfield from external $^{15}NH_4NO_3$ (Figure 2). The first two of the above resonances are a triplet and a doublet, respectively, with 90–80-Hz coupling constants, and the latter three peaks are singlets. They could be assigned to $^{15}NH_2$, $^{15}N^1$, $^{15}N^3$, $^{15}N^9$, and $^{15}N^7$, respectively, from the coupling pattern and by comparison with previous data of ^{15}N-GMP.[12] Upon single-frequency irradiation at 10.6 ppm in the proton resonance frequencies, the $^{15}N^1$ signal becomes a singlet. Therefore the above assignment for G-N^1H of the G·U base pair was confirmed. The $^{15}NH_2$ resonance at 52 ppm was also found to have very low intensity. This is due to negative NOE by the saturated amino proton transferred from the irradiated imino proton.

The intrinsic resonance positions of hydrogen-bonded U-N^3H and G-N^1H in tRNA have been estimated by Geerdes and Hilbers[13] to be 12.5 ± 0.1 and 12.2 ± 0.1 ppm, respectively, by comparing the observed data and calculated ring-current chemical shifts. The estimated chemical shifts according to their calculation (12.2 and 11.7 ppm) are quite different from those observed for the present tetramer. X-ray crystallographic study of this tetramer is now being undertaken.[14]

Registry No. G-G-C-Up, 75902-87-3; G*-G-C-Up, 83731-12-8; G, 73-40-5; U, 66-22-8.

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Four-Center Cyclic Transition States and Their Associated Deuterium Kinetic Isotope Effects: Hydrogenolysis of *n*-Octyllithium[1a]

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The temperature dependence of the kinetic isotope effect provides a delicate probe of selected transition-state qualities. Thus, for example, reactions that proceed through a rate-determining step that involves a linear hydrogen transfer are recognized by Arrhenius parameters of characteristic magnitude.[2,3] However, a controversy exists concerning the characteristic values for these parameters when hydrogen transfer occurs via a significantly nonlinear transition state. Theoretical considerations[4] of hydrogen isotope effects for such transition states as well as related calculations[5] suggest that there is no basis for expecting nonlinear transition states to result in a temperature-independent isotope effect or preexponential factor much larger than $\sqrt{2}$, the theoretical upper limit for linear H transfer. However, others[6] suggest that reactions that proceed through a rate-determining nonlinear hydrogen transfer are characterized by a hydrogen isotope effect that is temperature independent and an Arrhenius preexponential factor that is significantly greater than $\sqrt{2}$. Thus, a clear dichotomy exists. In an effort to resolve this ambiguity we have examined the temperature dependence of the kinetic isotope effect associated with a transition state in which the requirement of a significantly nonlinear hydrogen transfer is reasonably unequivocal.[7]

The hydrogenolysis of *n*-octyllithium[8a] proceeds readily and quantitatively in decane solution under an ambient pressure of hydrogen and at temperatures <100 °C. The kinetics for this reaction, which is pseudo first order in *n*–octylllithium, are summarized in Table I along with the corresponding data for the equivalent reaction with deuterium. Also summarized are the relevant data obtained under competitive conditions. Within experimental error, both independent and competitive reactions exhibit equivalent temperature dependencies.

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(1) (a) Supported by the NSF, Grant CHE 80-17045, and the DOE, Contract No. DE-AS05-80ER10662. (b) Postdoctoral Fellow, Consejo Nacional de Investigaciones Cientificas y Technicas de la Republica Argentina.

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Table I. Summary of Kinetic Deuterium Isotope Criterion for the Reaction of Hydrogen with *n*-Octyllithium[a,d]

$$n\text{-}C_8H_{17}Li + X_2 \xrightarrow[k_X]{n\text{-}C_{10}H_{22}} n\text{-}C_8H_{17}X + LiX$$
$$X = H, D$$

X_2	T, °C	10^5k_1,[b] s^{-1}	10^3k_2, M^{-1} s^{-1}	E_a, kcal/mol	A_X	$-\Delta S^{\ddagger}$, eu
H_2	50.0	1.018	3.461	11.06 ± 0.08	278 ± 1	47.4
	60.0	1.713	5.706			
	70.0	2.754	8.608			
	80.0	4.300	13.105			
D_2	50.0	0.620	2.108	12.27 ± 0.08	1099 ± 1	44.6
	60.0	1.103	3.673			
	70.0	1.867	5.836			
	80.0	3.089	9.414			

Competitive Determination

X_2	T, °C	k_H/k_D[c]	$[\Delta E]_D^H$	A_H/A_D	σ
H_2-D_2	50.0	1.642 ± 0.002[e]	1.253 ± 0.029	0.239 ± 0.012	0.999
	60.0	1.552 ± 0.004[e]			
	70.0	1.475 ± 0.003[e]			
	80.0	1.392 ± 0.002[e]			

[a] Initial composition: 0.450 M $[n\text{-}C_8H_{17}Li]_0$; a constant partial pressure of hydrogen (deuterium) was maintained throughout the course of the reaction (P_{H_2} = 988 mmHg). The corresponding concentration of hydrogen in solution was calculated accordingly.[20] [b] On the basis of the following expression; rate $= -k_1[RLi] = k_1[LiH]$. [LiH] was determined by monitoring manometrically the hydrogen produced by protonolysis with aqueous acid. The value of k_1 was obtained from a plot of ln $[H_2]/[H_2]_0$ vs. time (correlation coefficient 0.999). [c] The primary hydrogen–deuterium isotope effect for the competitive hydrogenolysis of *n*-octyllithium can be expressed as $k_H/k_D = [RD]/[RH]$. The latter ratio was determined by high-precision, whole-molecule mass spectrometry,[25] simultaneously monitoring (a total of 5000 scans was used) the M, M + 1, and M + 2 ions of the *n*-octane-d_0 and -d_1 mixture isolated at the completion of each reaction. Since *n*-octane exhibits no M − 1 ion, a correction for this factor was unnecessary. All values have been corrected for residual *n*-octane-d_0 present in each determination as a result of adventitious hydrolysis of the starting organolithium reagent. An ionizing voltage of 70 eV and a constant source pressure of 8.0 × 10^{-7} mmHg were employed. [d] Prepared by reaction of $(n\text{-}C_8H_{17})_2Hg$ with excess lithium dispersion in olefin-free decane. [e] 90% confidence level.

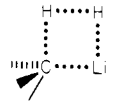

Figure 1. Idealized representation of the rate-determining transition state for the hydrogenolysis of *n*-octyllithium.

The data in Table I reveal a number of points pertinent to the mechanism of the hydrogenolysis of *n*-octyllithium. First, the order of the reaction with respect to alkyllithium reagent suggests that the rate-determining step involves the addition of hydrogen to a fully associated (probably hexameric) unit of *n*-octyllithium.[8b] Thus, prior dissociation of the dominant equilibrium structure into a more reactive, less associated intermediate species does not appear to be required.[9]

Second, we note that the rate of hydrogenolysis for alkali metal alkyls follows the order Cs > K > Li.[7,8] Also, addition of 1 equiv of the bidentate chelating ligand *N,N,N′,N′*-tetramethylethylenediamine accelerates the rate of alkyllithium hydrogenolysis by a factor of ca. 7000.[10a] This reactivity is increased even further when the bidentate chelating ligand is replaced by a tridentate ligand such as *N,N,N′,N′,N″*-pentamethyldiethylenetriamine.[10b] Taken together, these facts illustrate the dominant influence that the ionic character of the M–C bond exerts in determining the efficacy of the heterolytic cleavage of hydrogen. Most significantly, the rate of hydrogenolysis of lithium alkyls is significantly *reduced* in the presence of 1 equiv of the tetradentate ligand *N,N,N′,N′,N″,N″*-hexamethyltriethylenetetraamine, **2**.[10c] Such behavior is consistent with the requirement that hydrogenolysis proceeds through a concerted, four-center cyclic transition state, which cannot be achieved in this last instance because of the formation of solvent separated ion pairs.[10b]

Third, the kinetic behavior outlined in Table I parallels that observed for the homogeneous, bimolecular, heterolytic activation of hydrogen by metal ions[11] with two noteworthy differences. Specifically, the activation energy for the hydrogenolysis of *n*-octyllithium lies somewhat below the range (ca. 14–27 kcal/mol), and the entropy of activation is considerably greater than the range (−7 to −25 eu) reported for these reactions. We conclude that the very large, negative value of $\Delta S^{\ddagger}$ observed for the hydrogenolysis of *n*-octyllithium is a reflection of the highly organized,[12] unsolvated, polar transition state associated with this reaction.

Finally, the magnitude of the parameter $[\Delta E]_D^H$, which corresponds to the difference between the activation energy for the reaction with hydrogen and the corresponding value observed for the equivalent reaction with deuterium, is only slightly greater than the zero-point energy difference between H_2 and D_2, $[\Delta E_0]_D^H$ = 1.15 kcal/mol.[13] This fact suggests that tunneling, albeit not extensive, is nonetheless operative in the hydrogenolysis of *n*-octyllithium. It follows that a temperature-independent kinetic isotope effect is not a necessary criterion for characterizing transition states involving a four-center, cyclic hydrogen transfer. Indeed, these parameters are not significantly different from those associated with processes that purportedly proceed through a linear, three-center hydrogen-transfer transition.

Relevance to Catalysis. Previous studies have emphasized the essential requirements that govern the ability of a species to activate an electronically saturated molecule such as hydrogen.[11] The observations presented here are consistent with these conclusions and also suggest considerations that explain why a host of substances including hydroxide and amide ions[14,15] as well as

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(9) In instances where the dissociation of an associated organolithium reagent into less associated but kinetically more reactive intermediate species take place, kinetic studies have shown that a fractional order generally obtains with respect to the organolithium reagent and that this order is usually the reciprocal of the degree of association of the organolithium compound; see: Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: New York, 1974; pp 98–100.

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a variety of non-transition-metal oxides[16] can effect the heterolytic cleavage of molecular hydrogen and in some instances even serve as efficient hydrogenation catalysts.[16,17] If further follows that such considerations are most probably responsible for the ready hydrogenolysis of both main groups[21] as well as certain transition-metal–carbon σ bonds.[22-24]

Finally, although there can be no doubt of the unique role of d electrons in the activation of molecular hydrogen by many homogeneous and heterogeneous transition-metal catalysts,[17,18] the results and conclusions presented here suggest that attempts to associate patterns in metal–hydrogen reactivity solely through correlations in isoelectronic structure may be oversimplied since such reactivity clearly involves other factors as well.

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(17) So-called "oxidation addition" of hydrogen to various transition-metal complexes[18]

$$L_nM + H_2 \rightarrow L_nM(H)_2$$

represents another pathway for hydrogen activation. Although the kinetics of this process have been examined in some detail, there remains some ambiguity concerning their significance in terms of the detailed mechanism of these addition processes.[19] We suspect that the unusually low isotope effect ($k_H/k_D = 1.22$)[19] associated with the addition of hydrogen to $IrCl(CO)(Ph_3P)_2$ may also be a consequence of the cyclic three-center transition-state geometry of the purported activated complex. Studies aimed at clarifying this point are in progress.

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Midinfrared Vibrational Circular Dichroism Studies of Cyclophosphamide and Its Congeners

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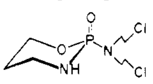
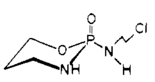
Vibrational circular dichroism (VCD) is the measurement of the difference in absorption of left and right circularly polarized infrared light by vibrational transitions of chiral molecules.[1] Several studies have noted correlation of the sign of the VCD (or that of its Raman analogue) for certain diagnostic bands with molecular configuration[2] or conformation[3] in solution. The availability of a large number of resolved bands that are often characteristic of localized parts of a molecule gives VCD the potential of offering new insights into the stereochemistry of a variety of different molecular systems.

We report here preliminary VCD results for four organophosphorus compounds: 2-[bis(2-chloroethyl)amino]tetrahydro-2*H*-1,3,2-oxazaphosphorine 2-oxide (cyclophosphamide, I);



(−)-S-I



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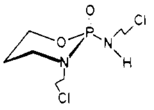
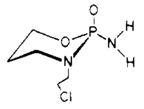


(+)-R-II



(+)-R-IV

2-((2-chloroethyl)amino)-3-(2-chloroethyl)tetrahydro-2*H*-oxazaphosphorine 2-oxide (ifosphamide, II); 2-((2-chloroethyl)-amino)tetrahydro-2*H*-1,3,2-oxazaphosphorine 2-oxide (III); 2-amino-3-(2-chloroethyl)-tetrahydro-2*H*-1,3,2-oxazaphosphorine 2-oxide (IV). Racemic forms of compounds I and II are clinically useful anticancer drugs while compounds III and IV are metabolites of II.[4] The stereospecific synthesis and assignment of the absolute configurations of I–III have been published.[5,6] Absolute configuration of IV was assigned by means of stereochemical correlation. Thus it was of interest to utilize compounds I–IV as models for studies of the applicability of VCD to organophosphorus structure.

Our focus is on those vibrations that contain significant contributions from the P–O and P=O bonds. We have found what appears to be a "VCD marker mode" for the absolute stereochemistry about phosphorus. Such a correlation is not possible with optical rotation[5] and ORD CD studies[7]. In addition, this is one of the first reports of VCD in the 1000-cm^{-1} (10 μm) region.[8,9]

The optical isomers of the compounds I–IV, were prepared by our previously published methods.[5a,6] Optical rotations obtained were as follows: (+)-(*R*)-I, $[\alpha]^{25}{}_D$ +2.3° (c 3, CH_3OH); (−)-(*S*)-I, $[\alpha]^{25}{}_D$ −2.3° (c 3, CH_3OH); (+)-(*R*)-II, $[\alpha]^{25}{}_D$ +44.0° (c 2, CH_3OH); (−)-(*S*)-II, $[\alpha]^{25}{}_D$ −39.0° (c 4, CH_3OH); (−)-(*R*)-III, $[\alpha]^{25}{}_D$ −15.1° (c 3, CH_3OH); (+)-(*S*)-III, $[\alpha]^{25}{}_D$ + 15.1° (c 3, CH_3OH); (+)-(*R*)-IV, $[\alpha]^{25}{}_D$ +16.1° (c 3, CH_3OH), (−)-(*S*)-IV, $[\alpha]^{25}{}_D$ −18.0° (c 3, CH_3OH).

VCD and absorption spectra were obtained on the UICC spectrometer.[1a] Extentions to our optical configuration[10] along with spectra of a variety of other molecules in the 10-μm region are detailed elsewhere.[9] Spectra were run on solution samples placed in a demountable cell having two NaCl windows separated by Teflon spacers. Solvents used included CS_2, CH_2Cl_2, and CH_3CN. The noise level of spectra run on samples in CH_3CN

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