Motional Collapse of Methyl Group Vibrational Bands

Sir:

N-Alkanes such as hexadecane form clathrate crystals with urea in which the alkane chains are held in their fully extended all-trans conformation in channels formed by the urea matrix.[1] The chains are arranged end to end in the channels with adjacent methyl groups. The neat alkane crystals also have extended chains which are arranged in a similar manner, although of course the lateral surroundings of the chains are quite different.

The C-H stretching bands of the alkanes are easily observable in both the infrared and the Raman spectra even in the clathrate, since urea has essentially no bands in this region. The C-H bands are similar in the clathrate and in the neat crystal and the normal modes corresponding to the major bands are fairly well characterized. In the infrared spectrum at room temperature, the hexadecane-urea clathrate shows the doubly degenerate asymmetric stretch with a half-width at half-maximum of ~11 cm^{-1} at 2956.6 cm^{-1}.[2] At 9 K the spectrum is dramatically different: the asymmetric stretch appears as two bands at 2946.1 (with a half-width of 4 cm^{-1}) and 2958.4 cm^{-1} (with a half-width of 8 cm^{-1}). As the temperature is raised from 9 K, the asymmetric stretching bands gradually collapse in a manner qualitatively the same as the collapse of an exchanging nuclear magnetic resonance doublet.

The spectra can be analyzed using the Bloch equations with exchange, modified for the fact that the low-temperature doublet consists of two bands of unequal intensity and width. These Bloch equations give

$$I(\omega) = \operatorname{Im} \frac{i\tau[I_+(\alpha_-\tau + 1) + I_-(\alpha_+\tau + 1) + 2(I_+I_-)^{1/2}]}{(\alpha_+\tau + 1)(\alpha_-\tau + 1) - 1}$$

using the notation familiar from NMR.[3] Here $I(\omega)$ is the intensity of the line, ω_0 is the center of the spectrum, τ is the reciprocal rate of exchange, $\alpha_\pm = 1/T_\pm - i(\omega - \omega_0 \mp \delta\omega/2)$ and $I_\pm$, $T_\pm$, and $\delta\omega$ are the intensities, the dephasing times (taken as the inverse widths), and the splitting of the two bands in the absence of exchange, respectively. The cross term $(I_+I_-)^{1/2}$ is due to the "overlap" contributions;[4] similar formulas for exchange collapse of spectral lines have been derived before.[5] The infrared spectra were analyzed by fitting each spectrum with a set of Lorentzian bands and then comparing the peak splittings of the asymmetric methyl stretching bands with those calculated from the equation for different values of τ. Values of $I_\pm$, $T_\pm$, and $\delta\omega$ were taken from the 9 K spectrum which is assumed to represent the no exchange situation. The values of τ can be fit to an Arrhenius expression $\tau = A \exp(-\Delta E/kT)$ which gives $A = 0.88 \pm 0.15$ ps and $\Delta E = 55 \pm 9\ \text{cm}^{-1}$. We have measured Raman spectra from 130 K to room temperature and, over this range, these spectra look similar to the infrared spectra.

The infrared spectra of a neat polycrystalline sample of $n\text{-C}_{20}\text{H}_{42}$ show narrower bands at low temperature but otherwise behave in a similar manner to the clathrate spectra. They have been analyzed in the same way with the result $A = 1.46 \pm 0.10$ ps and $\Delta E = 60 \pm 5\ \text{cm}^{-1}$.

It is known that the bands which we are considering are split by intramolecular effects[6] and that the higher frequency one is due to the mode symmetric with respect to the plane of the carbon skeleton.[7] NMR studies of neat alkane crystals suggest that at temperature of ~150 K, the methyl groups reorient freely while the backbone methylene groups are held rigidly.[8] In contrast, the methylene backbone seems to be considerably more mobile in the clathrate crystals.[9]

The motional collapse we observe is similar in the two systems and is almost certainly due to the rotation of the methyl groups. The high temperature rate (the A factor) of ~1 ps is reasonable for this motion. The activation energy of ~60 cm^{-1} is apparently low for a barrier which is thought to be 910 cm^{-1} in the neat crystal.[8] The rotational tunneling or other exchange mechanism is certain to be dependent on the torsional state and thus on the temperature. Thermally weighted tunneling times show rather low activation energies at low temperatures[10] and this may be the qualitative explanation of our low values.

The motional collapse of vibrational lines should generally be observable for rapidly rotating methyl groups, librating water molecules and other hydrides. Indeed, spectra of the water of hydration of a variety of alkali and alkaline earth salts show similar collapsing bands.[11] In these crystals, the water sits in one of two asymmetric sites at low temperature, and moves between them as the temperature is increased.

The existence of these collapsing bands is of interest to the general theory of motional narrowing of vibrational bands[4,12] and provides a way to determine the fast motions of small groups in solids. We are in the process of studying both the alkane and water of hydration systems further to better characterize these processes.

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Electron Transfer in Nickel-Catalyzed Addition Reactions

Sir:

We recently noted that Ni(acac)_2 treated with 1 equiv of Dibah efficiently catalyzed conjugate addition of alkenyl[1] and alkynyl[2] organometallics to α,β-unsaturated ketones. Based on product analysis arguments, House has made a case for an electron-transfer mechanism for cuprate conjugate additions to α,β-enones.[3] In the light of his correlations, we have attempted to determine if the Ni(acac)_2/Dibah system could serve as a one-electron reducing agent and if conjugate addition using this system occurred by electron transfer. We now report our results, based on chemical and electrochemical studies, which substantiate these contentions.

As a preamble to our studies we measured the catalytic activity of the Ni(acac)_2/Dibah system per unit of time over a period of 24 h. The catalyst mixture was prepared in the usual manner and was allowed to stir at 0 °C. At various time intervals, aliquots were withdrawn and were tested for relative ability to catalyze the conjugate addition of alkenylzirconium reagent **1** to cyclohexen-1-one (as measured by yield of adduct produced in a given 15-min period). We noted that catalytic

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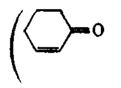
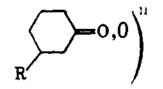
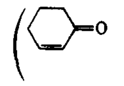
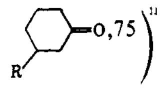
Table I. Ni-Catalyzed Coupling of Aryl Halides with Alkenylzirconium Species

catalyst	$E_{1/2}$ (vs. SCE, THF)	ArX	reaction conditions, °C, h	yield,[a] %
Ni(acac)$_2$ + Dibah + 4PPh$_3$ (Negishi)	−0.40		0, 3	(quant)
			20, 12 0, 3	(quant) 0
			0, 5	0
			0, 3	 [11]
Ni(PPh$_3$)$_4$	−0.41 (Kochi)			
Ni(acac)$_2$ + Dibah	−1.8, −1.30		0, 3	70
			0, 5	10
			0, 3	 [11]

[a] Yields in parentheses were determined by VPC; all other yields are for isolated product.

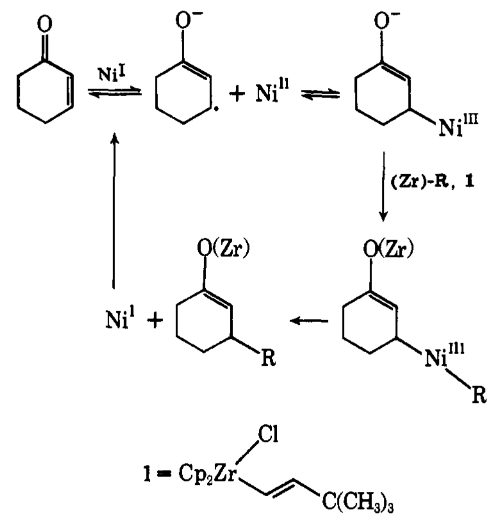
activity (as a function of digestion time) increased to a maximum after ~6 h and then decreased to very low activity after an ~24-h digestion.

An electron-transfer mechanism implies that the catalyst can readily transfer an electron to the organic substrate. Assuming that electron transfer is the rate-determining step in the catalytic cycle, the rate of one-electron reduction of the substrate should correlate with the efficiency of catalysis. A lower oxidation potential for the catalyst should result in faster electron transfer.[4] Cyclic voltammetry (CV) experiments were therefore performed on the Ni(acac)$_2$/Dibah system (in THF vs. SCE). The catalyst (1 mM) was prepared in the electrochemical cell (in the presence of 0.5 M n-Bu$_4$NClO$_4$ as supporting electrolyte). At various time intervals CV measurements were made. Four distinct oxidation waves (−1.8, −1.30, −0.50, +0.57 V vs. SCE; all measurements were ±0.02 V) were detected during the course of the experiment (24 h at 23 °C). Only one reduction wave was observable (−1.75 V). Wave clipping experiments showed that the waves at −1.8, −1.30, and −0.50 V were all coupled to the cathodic one at −1.75 V.[5] The correlation between catalytic activity and these CV (lowest oxidation potential) measurements is telling. Specifically, the buildup and decay of the most easily oxidized species observed paralleled the rise and fall of catalytic activity of the system determined as described above. For example, the (anodic) wave at −1.8 V disappeared within 1 h. The wave at −1.30 V grew during this time but began to diminish after 8 h. The wave at −0.50 V was no longer observed after 8 h, but the one at +0.57 V, barely observable on initial scans, grew in relative intensity. After 24 h only the +0.57- and −1.30-V waves were observable in the anodic scan.

A corollary investigation was performed to provide a more definitive demonstration of the Ni(acac)$_2$/Dibah system as an electron-donating reagent in a catalytic sequence. It has been shown that nickel complexes effect coupling reactions of aryl halides and various electropositive organometallic reagents in both stoichiometric and catalytic sequences, for example, Negishi's discovery of nickel-catalyzed coupling of aryl halides and alkenylzirconium reagents.[6] In this sequence an arylnickel(II) species is formed by oxidative addition of aryl halide to a low-valent nickel complex [here, in situ generated (PPh$_3$)$_4$Ni].[6] Since no buildup of the arylnickel(II) compound is observed, it is likely that oxidative addition of aryl halide determines the overall rate of catalysis in the coupling sequence. In an elegant series of mechanistic investigations, Kochi has elucidated the oxidative addition reaction between aryl halides and reduced Ni species and has found it to proceed by an electron-transfer mechanism.[4] Electron transfer between the Ni species and the aryl halide is rate determining and CV measurements made on various Ni(0) complexes could be used to correlate ease of electrochemical oxidation of these Ni(0) complexes with rates of aryl halide oxidative addition to them.[4] Comparative CV measurements on Negishi's catalyst[6] and on Ni(acac)$_2$/Dibah should enable prediction of *relative* catalytic efficiency of these two systems. As can be seen from the data in Table I, the higher catalytic activity of the Ni(acac)$_2$/Dibah system vs. L$_4$Ni does indeed correlate with CV measurements. Noteworthy then is the observation that L$_4$Ni does *not* catalyze conjugate addition of **1** to cyclohexenone, an observation consistent with the notion of electron transfer as the rate-determining step in this reaction.

Postulating initial reduction of substrate by electron transfer in catalytic coupling cycles suggests that the Ni(acac)$_2$/Dibah system involves a reduced oxidation state of Ni. Certainly the use of organoalanes to reduce Ni(II) to Ni(0) (in the presence of trapping ligands) is a classical method for the preparation of complexes of Ni(0).[7] Ni(acac)$_2$ is reduced by Dibah via ligand exchange of acac ligands on Ni for hydride and isobutyl groups on Al, and isobutane and isobutene are evolved.[8] It is possible to determine the bulk oxidation state of nickel by following isobutane evolution; formation of 1 mol of isobutane results in an oxidation-state change of two units per mole of Ni (formation of isobutene does not affect the oxidation-state calculation). An initial burst of isobutane (0.5 equiv) occurs

Scheme I. Proposed Mechanism for Conjugate Addition



immediately upon mixing Ni(acac)$_2$ with 1 equiv of Dibah. This is followed by a much slower evolution of an additional 0.5 equiv of isobutane. Or, reaction between Ni(acac)$_2$ and Dibah results in a rapid oxidation-state change from Ni(II) to Ni(I) followed by gradual reduction to Ni(0). When compared with this isobutane evolution data, it becomes clear that the reduction of Ni(II) to Ni(0) is associated with the *loss* of catalytic activity for the system.

On the basis of the data presented, Ni-catalyzed conjugate addition of alkenylzirconium compounds to enones likely involves initial electron transfer from a Ni(I) species to the unsaturated ketone (Scheme I). Attack of ketyl upon the Ni(II) species thus generated yields an organonickel(III) intermediate which could undergo transmetalation with the alkenylzirconium compound and reductive elimination to give the observed zirconium enolate and regenerate Ni(I). It is interesting to note here that Kochi has recently determined that the transformation Ni(I) → Ni(III) → Ni(I) is responsible for efficient catalysis in nickel-mediated aryl coupling reactions.[9]

The CV experiments described above suggest that catalysis of conjugate addition occurs through a family of nickel species, the members of which possess different lifetimes and different oxidation potentials. The fact that a *single* reduction wave couples the three reducing waves observed in the anodic scan indicates that a *single* oxidation state describes the Ni species in this family (it may be that the various species observed reflect clustering in which aggregation numbers or geometries for Ni atoms in the various members of the family are different). The fact that *none* of the reducing species observed (in the presence of the supporting electrolyte) are strong enough reducing agents to add an electron to an *isolated* α,β-enone suggests that complexation between that unsaturated organic molecule and the reactive Ni species may be important.[10,11] Preliminary attempts were made at isolating an active nickel catalyst by allowing reduction of Ni(acac)$_2$ with Dibah in THF to proceed for 24 h. Evacuation of solvent left a black solid material which exhibited a CV anodic wave at -1.30 V and a cathodic wave at -1.75 V. The black material successfully catalyzed the conjugate addition of **1** to cyclohexen-1-one. Further investigations using this material hopefully will shed more light on the nature of these coupling reactions.

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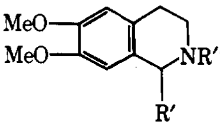
Photohydrolysis of Sulfonamides via Donor–Acceptor Ion Pairs with Electron-Donating Aromatics and Its Application to the Selective Detosylation of Lysine Peptides

Sir:

The importance of exciplexes in photochemistry is now well recognized through a number of recent theoretical and mechanistic studies,[1] because they have opened the possibility of "endothermic photosensitization" in classical energy transfer.[2] As part of our photochemical studies[3] we report an improved photochemical removal of an *N*-tosyl protecting group from *p*-toluenesulfonamides with the assistance of electron-donating aromatic compounds.[4] This reaction is of mechanistical interest and also may provide a useful method in organic synthesis, especially in peptide chemistry.

In 1969, Umezawa et al. reported that, on irradiation in the presence of NaBH$_4$, 1-substituted 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline *N*-tosylates (**1a–d**) were readily cleaved to the corresponding tetrahydroisoquinolines (**2a–d**) in high yields.[5] The photolysis was proceeded via intramolecular formation of an excited donor–acceptor pair between the electron-donating dimethoxybenzene group and the electron-withdrawing tosyl group.[6] Extension of this photolysis to intermolecular reactions may provide a general method for the cleavage of sulfonamides.



1a, R' = H; R'' = Ts	**2a**, R' = R'' = H
b, R' = Me; R'' = Ts	**b**, R' = Me; R'' = H
c, R' = Ph; R'' = Ts	**c**, R' = Ph; R'' = H
d, R' = CH$_2$Ph; R'' = Ts	**d**, R' = CH$_2$Ph; R'' = H

When an EtOH solution of *N*-tosylmethylphenethylamine (**3**, 10 mM) and veratrol (**12**, 30 mM) was irradiated with a 100-W high-pressure mercury lamp, methylphenethylamine (**5**) was isolated in 66% yield. Irradiation in the presence of a large excess of NaBH$_4$ (0.1 M) in 80% aqueous EtOH improved the yield to 86%.[7] Similarly, **4** and **7** readily gave **6** and **8**, respectively (Table I).

In Table II the $k_q\tau$ values calculated from linear Stern-Volmer plots of fluorescence quenching of dimethoxybenzenes (**12, 13**) by *N*-tosylmethylamine,[8] relative quantum yields for disappearance of **3** (ϕ), and oxidation potentials [$E_{1/2}$ (ox)]

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