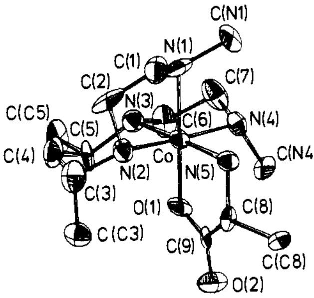

Figure 2.

boxylation solution were Λ-β_2-[Co(*R*-Ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$(ClO_4)_2 \cdot H_2O$ crystals.

The third step is the release of alanine from the complex and recovery of the carbonato complex. The recoveries were 88% for the DNP-alanine and 64% for the carbonato complex. The specific optical rotation of the DNP-alanine obtained here indicated a mixture of *R* and *S* isomers in the ratio 83:17.[11] This optical yield is fairly high compared with the reported results.[2]

The last step in the asymmetric synthesis is to regenerate the starting *trans*-dichloro complex from the carbonato complex. Treatment of the carbonato complex with concentrated HCl produced the expected *trans*-dichloro complex.[7] The most important reaction in this cyclic system is the release of alanine from [Co(Ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ ion under mild conditions.

To confirm the structure of this complex cation, we previously determined the structure of $(-)_{546}$-Λ-β_2-[Co(*R*-Ala)-(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$Br_2 \cdot 3H_2O$ by an X-ray crystallographic study.[9] The absolute configuration of the complex cation is Λ in the β_2 form, and the alanine coordinates to cobalt ion with bidentate (Figure 2). Bond distances and angles were quite usual.

Quite recently, the release of alanine was also observed for an alaninato complex of 2*R*,4*R*,9*R*,11*R*-Me_4-3,2,3-tet.[12] The first absorption bands of alaninato complexes containing 5*R*,7*R*-Me_2-2,3,2-tet,[13] 2*R*,4*R*,9*R*,11*R*-Me_4-3,2,3-tet, and 1,5*R*,7*R*,11-Me_4-2,3,2-tet shifted by 200, 600, and 700 cm^{-1} to lower energy, respectively, as compared to that of 2,3,2-tet[14] complex. For both the alaninato complexes of 2,3,2-tet and 5*R*,7*R*-Me_2-2,3,2-tet, the release of alanine has not been observed but racemization of alanine of the complex has been observed. Therefore we consider the labile feature of the alaninato complex containing 1,5*R*,7*R*,11-Me_4-2,3,2-tet or 2*R*,4*R*,9*R*,11*R*-Me_4-3,2,3-tet relates closely to the strength of the ligand field. Consequently, many inert cobalt(III) complexes might be activated to be catalysts for the asymmetric synthesis of α-amino acids by the modification of ligands so that they could produce an appropriate ligand field.

We also found that glycine and valine were released from the corresponding amino acidato complexes of 1,5*R*,7*R*,11-Me_4-2,3,2-tet. Accordingly, the present asymmetric synthesis depicted in Figure 1 could be practically applied to the synthesis of expensive and naturally rare α-amino acids by variation of aminoalkylmalonic acids.

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Supplementary Material Available: Final positional and thermal parameters, bond distances, and bond angles (4 pages). Ordering information is given on any current masthead page.

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(10) The decarboxylated solution also contained the minor (*S*)-alaninato complex.

(11) The specific optical rotation of the solution was observed at 546 nm, and the concentration of the same solution was calculated from the extinction coefficient at 360 nm (ϵ 1.72 × 10^4). Authentic DNP-(*S*)-alanine: $[\alpha]_{546}$ +221° (1% $NaHCO_3$).

(12) The fully systematic name is (2*R*,4*R*,9*R*,11*R*)-4,9-dimethyl-5,8-diazadecane-2,11-diamine.

(13) The fully systematic name is (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine.

(14) The fully systematic name is 3,7-diaza-1,9-nonanediamine.

Observation of an Unprecedented Heavy-Atom Effect on the Rate of $^1n,\pi^* \rightarrow {}^3n,\pi^*$ in a β,γ-Unsaturated Ketone[1]

Lidia T. Calcaterra and David I. Schuster*

Department of Chemistry, New York University
New York, New York 10003

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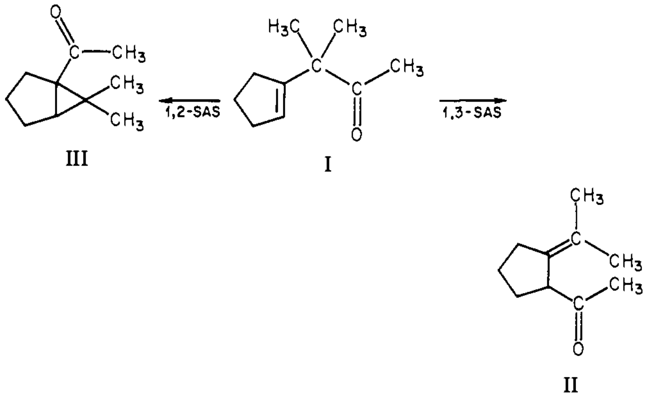
Wagner[2] experimentally demonstrated that heavy-atom solvents have no effect on the intersystem crossing rate of alkanones. This supported El-Sayed's earlier calculations[3] on $\pi^* \rightarrow n$ transitions of X_2CO (X = halogen) which suggested that further enhancement of the already large rates of $S \rightleftharpoons T$ transitions in "pure" n,π^* states (due to effective spin-orbit coupling) by internal heavy atoms should be negligible, although it should be noted that calculations by Carroll et al.[4] predict a substantial internal heavy-atom effect (HAE) on phosphorescence lifetimes of X_2CO due to considerable delocalization of the oxygen n electron. Morrison[5] has shown that an external heavy atom can affect the photochemical behavior (dimerization) of coumarin, an unsaturated carbonyl compound, although the heavy atom does not effect the triplet yield but rather perturbs later stages of the dimerization mechanism.

We present experimental evidence that the n,π^* excited singlet of 3-(1-cyclopentenyl)-3-methyl-2-butanone (I) is sensitive to an external HAE. It has been previously observed[6] that direct irradiation of I gives the 1,3-sigmatropic acyl shift (1,3-SAS) product II and other products, while acetone sensitization affords II as well as the product (III) of a 1,2-sigmatropic acyl shift (1,2-SAS) or oxa-di-π-methane (ODPM) rearrangement. These results were confirmed in the present study. We have further been able to demonstrate that the formation of II occurs from both S_1(n,π^*) and T_2(n,π^*) states, the former populated on direct light absorption and the latter under conditions of triplet sensitization, while III arises exclusively from the $T_1(\pi,\pi^*)$ state. These assignments are based on differential sensitization and quenching results, and the inverse temperature dependence of the fluorescence yield and the quantum efficiency of the 1,3-SAS ($\Phi_{1,3}$).[7]



Irradiation of I (purified by preparative high-pressure liquid chromatography) under 2.2 atm of xenon resulted in a 21 ± 1% decrease in its fluorescence intensity (see Figure 1), while the efficiency of formation of the 1,3-SAS product ($\Phi_{1,3}$) increased from 0.058 ± 0.006 to 0.072 ± 0.007. The fluorescence intensity decrease[8] was observed in three runs by using two different samples, while more modest and less precise enhancements in $\Phi_{1,3}$

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(8) There was no measurable change in the optical density of the solutions upon addition of xenon; the UV absorption and fluorescence spectra also showed no change in either shape or position (see Figure 1).

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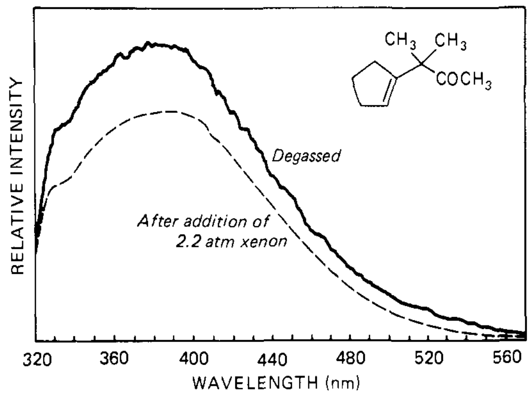

Figure 1. Fluorescence of I in spectrograde cyclohexane in the absence (solid line) and presence (dashed line) of 2.2 atm of xenon.

were observed several times at lower xenon pressures before the data given above were acquired using a specially constructed cell which could withstand higher xenon pressures. The formation of III on direct excitation of I was observed neither in the presence or absence of xenon. Furthermore, the ratio of the yields of II and III on acetone sensitization was unchanged (3.8 ± 0.2) in the presence of 2.1 atm of xenon in parallel irradiations under conditions where acetone absorbed virtually all the incident radiation (0.01 M solutions of I).

The inverse correlation between fluorescence intensity and $\Phi_{1,3}$ brought about by xenon perturbation can be explained by an increase in the rate of intersystem crossing (ISC) from $S_1(^1n,\pi^*)$ to $T_2(^3n,\pi^*)$, which reacts to give the 1,3-SAS. The fact that xenon does not affect the formation of III on acetone-sensitized excitation of I indicates that the T_1 state of I is not quenched by 2.1 atm of xenon. Therefore, it appears that xenon selectively enhances the rate of the conversion from S_1 to T_2 and not to T_1. Furthermore, T_2 appears to react rapidly to the virtual exclusion of radiationless decay to T_1. The very low quantum efficiency of formation of III on acetone sensitization (0.027 ± 0.003) allows for some uncertainty in these conclusions, although the role of the T_1 state on direct light absorption by I in the presence or absence of xenon must be slight, on the basis of the limits of detection of III by GLC analysis. The low quantum efficiencies for formation of both II and III under various conditions (<20% total) are attributed tentatively to reversion to I from radical pair and diradical intermediates en route to II and III, respectively.[7]

The rate constant for the quenching of the fluorescent singlet excited state by xenon (k_q) can be obtained from the Stern–Volmer equation: $(I_f)_0/(I_f)_{Xe} = 1 + k_q\tau_s[Xe]$. One can derive a value for k_q of $1.38 \pm 0.6 \times 10^9$ M^{-1} s^{-1} by using the measured fluorescence lifetime of *I* of 0.4 ns,[9] a concentration of xenon of ca. 4.5×10^{-1} M calculated from the solubility of Xe in cyclohexane,[10] and the observed 21% decrease in the fluorescence intensity upon addition of 2.2 atm of Xe. This is as large as the quenching constant found by Horrocks et al.[11] for the most susceptible polyaromatic hydrocarbons.

Other investigators have also looked for a HAE in β,γ-unsaturated ketones (β,γ-UKs).[12,13] Recently Chae and Givens[13] have reported the decrease upon halogen substitution of the efficiencies of fluorescence and photoreaction of bicyclo[3.2.1]oct-2-en-7-ones. Although they ascribed it to an enhancement of radiationless decay from the singlet state, their data do not rule out the possibility of enhanced intersystem crossing to $^3n,\pi^*$ which then undergoes the 1,3-SAS reaction.

The selective population of the $T_2(n,\pi^*)$ state of *I* from S_1 $(^1n,\pi^*)$ under the conditions of xenon perturbation, and perhaps also to some extent in the absence of xenon,[7] is in apparent violation of the oft-stated selection rule[14,15] that intersystem crossing with carbonyl compounds should preferentially occur between singlet and triplet states of different configurations. The "allowed" transition in the present case should then be from $S_1(n,\pi^*)$ to $T_1(\pi,\pi^*)$. The observed "violation" could be due to the well-known interaction of the carbonyl and olefinic chromophores in β,γ-UKs which results in singlet and triplet excited states of mixed character.[16] A referee has raised the question of whether El-Sayed's rules[3,14] apply to bichromophoric molecules in general, and β,γ-UKs in particular, although it has also been suggested that the rules should have general applicability.[15]

The measured fluorescence lifetime of *I* of 0.41 ns[9] is actually shorter than that of alkanones[17] for which such heavy-atom effects have not been demonstrated.[2] However, the generality of the HAE for β,γ-UKs remains to be demonstrated. While a similar decrease was obtained in the fluorescence intensity of 2,2,4,4-tetramethylcyclohepta-3,5-dienone (relevant quantum yields of reaction were not measured), the fluorescence intensity of 7-*tert*-butylbicyclo[3.2.0]hept-6-en-2-one remained unchanged. These results indicate that correlating the HAE with other photochemical and photophysical properties of β,γ-unsaturated ketones as a function of molecular geometry may lead to greater insight into the chemical and physical properties of their photoexcited states.

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Modeling Heterogeneous Catalysts with Homogeneous Catalysts. Comparison of Catalytic Exchange of Deuterium for Hydrogen at the α and β Positions of Tertiary Amines by Using Either Palladium Black or $Ru_3(CO)_{12}$

Y. Shvo,[†] D. W. Thomas, and R. M. Laine*

Physical Organic Chemistry Department, SRI International
Menlo Park, California 94025

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The complexities arising from the chemical and physical interactions of heterogeneous catalyst surfaces with reactants and products makes mechanistic studies of heterogeneous catalytic reactions extremely difficult to perform. The reason is that these interactions are not particularly amenable to spectroscopic and kinetic analysis except in special cases.[1] In contrast, homogeneous catalysis reactions are amenable to study via a variety of incisive techniques available to the solution kineticist. Mechanistic studies of homogeneous catalytic or stoichiometric reactions of mononuclear and, recently, polynuclear organometallic complexes have made it possible to draw mechanistic analogies to similar reactions occurring on heterogeneous catalysts.[2,3] In fact, it has become commonplace to use organometallic reaction mechanisms to de-

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[†] On sabbatical leave from Tel Aviv University.

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