

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 $1.38 \pm 0.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by using the measured fluorescence lifetime of I of 0.4 ns,⁹ a concentration of xenon of ca. $4.5 \times 10^{-1} \text{ M}$ 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 Givens¹³ 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 vio-

lation 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 ns⁹ is actually shorter than that of alkanones¹⁷ 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 $\text{Ru}_3(\text{CO})_{12}$

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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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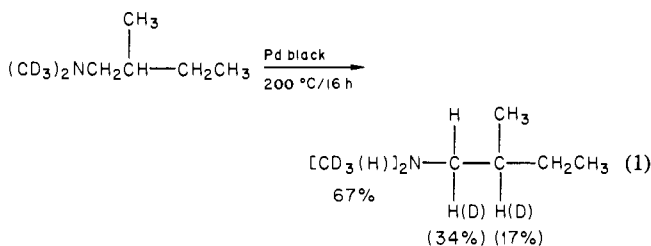
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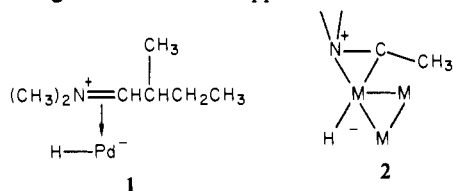
scribe mechanisms for heterogeneous catalytic reactions. These mechanistic analogies can be of considerable value if they result in the development of new, more efficient catalysts or the improvement of existing catalysts.

What is not commonplace with these analogies is to find correlations between homogeneous and heterogeneous catalytic reactions that extend to more than a few related steps in the respective catalytic cycles. We describe here the catalytic activation of the α and β C-H bonds of triethylamine (Et_3N), tri-*n*-propylamine (Pr_3N), and tri-*n*-butylamine (Bu_3N) with the heterogeneous catalyst, palladium black, and several homogeneous catalysts deriving from group 8 metal carbonyl complexes. The homogeneous catalysts, in particular the system based on $\text{Ru}_3(\text{CO})_{12}$, can be used to model the catalytic actions of palladium black for five different reaction parameters in two related catalytic reactions.⁴

We have previously reported the $\text{Rh}_6(\text{CO})_{16}$ acts as a precursor to a catalyst that activates the α and β C-H bonds of Et_3N or Pr_3N for deuterium exchange where D_2O serves as the source of deuterium.⁵ At that time we proposed a cluster-catalyzed mechanism involving C-H insertion to product a coordinated iminium ion (or ylide). Prior to our observation of the homogeneous rhodium-catalyzed deuterium for hydrogen exchange, Murahashi had reported⁶ several reactions of tertiary amines catalyzed on palladium black. For example:



Murahashi's proposed mechanism for deuterium transfer involves an iminium ion/palladium complex (1) similar to the intermediate 2 proposed in the rhodium-catalyzed deuterium for hydrogen exchange. Because of the apparent mechanistic similarities



between Murahashi's heterogeneously catalyzed reactions and the homogeneous rhodium-catalyzed reaction, we suggested that it might be possible to model the palladium-black-catalyzed deuterium for hydrogen exchange with the rhodium-catalyzed reaction.⁵

We have since found that $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, and $\text{Ir}_4(\text{CO})_{12}$ are also precursors to species that catalyze deuterium for hydrogen exchange on tertiary amines. Furthermore, the ruthenium catalyst appears to be a better model of Pd black than the rhodium catalyst (vide infra).

In several studies with $\text{Ru}_3(\text{CO})_{12}$, we have found that the deuterium for hydrogen exchange site selectivities (α vs. β) correspond closely to those found for Pd black (see Table I) for the three tertiary amines Et_3N , Pr_3N , and Bu_3N investigated. Moreover, the patterns of substitution for each tertiary amine are

(4) Reaction parameters are defined as independent observable aspects of the subject catalytic reaction(s). For example, product selectivity and catalyst activity are different reaction parameters.

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Table I. Catalytic Deuterium for Hydrogen Exchange on Tertiary Amines. Site Selectivities (α : β Ratios) for Various Catalysts^a

	Et_3N	Pr_3N	Bu_3N
$\text{Rh}_6(\text{CO})_{16}$ ^b	0.25:1	0.33:1	
$\text{Ru}_3(\text{CO})_{12}$ ^c	0.29:1	1.30:1	2.1:1
Pd black ^{d,e}	0.38:1	0.80:1	1.6:1 (4:1) ^f
Rh black			4:1 ^f

^a The values shown represent α : β site selectivity ratios determined by ^2H NMR as described in ref 5. ^b Reaction conditions and data from ref 5. ^c Reactions were run at 150°C for 20 h under 400 psi of CO . Reaction solutions contained 6.0 mL of amine, 0.1 mmol of catalyst precursor, and 100 mmol of D_2O . ^d Reaction conditions are as in c but with 2.0 mmol of Pd black under 100 psi of N_2 . ^e Pd black is recovered quantitatively. ^f Data from ref 6b; reactions were run at 200°C .

Table II. Patterns of Deuterium for Hydrogen Exchange for Various Group 8 Metals and Tertiary Amines and Relative Catalytic Activities^{a,b}

catalyst	turnover frequency for amine ^c			
	$\text{Et}_3\text{N}-d_1$	$\text{Et}_3\text{N}-d_2$	$\text{Et}_3\text{N}-d_3$	$\text{Et}_3\text{N}-d_4$
$\text{Rh}_6(\text{CO})_{16}$ ^d	β (0.5)	β (1.4)	β (5.6)	α (9.5)
$\text{Ir}_4(\text{CO})_{12}$ ^e	? (3.5)	? (2.5)	? (1.1)	? (0.9)
$\text{Ru}_3(\text{CO})_{12}$	α (0.6)	β (1.9)	β (4.9)	β (6.05)
$\text{Os}_3(\text{CO})_{12}$ ^f	β (0.6)	β (1.9)	β (4.9)	α (6.05)
Pd Black	α (0.5)	β (0.7)	β (1.2)	β (2.6)
	α (0.6)	β (1.2)	β (3.3)	β (4.6)
	$\text{Pr}_3\text{N}-d_1$	$\text{Pr}_3\text{N}-d_2$	$\text{Pr}_3\text{N}-d_3$	
$\text{Rh}_6(\text{CO})_{16}$ ^d	β (0.3)	β (0.7)	α (1.6)	0.4
$\text{Ru}_3(\text{CO})_{12}$	α (15.0)	β (8.0)	β (5.0)	5.0
Pd Black	α (5.5)	β (2.6)	β (2.1)	0.08
	$\text{Bu}_3\text{N}-d_1$	$\text{Bu}_3\text{N}-d_2$	$\text{Bu}_3\text{N}-d_3$	
$\text{Ru}_3(\text{CO})_{12}$ ^g	α (20.9)	β (8.3)	β (3.1)	8.4
Pd Black	α (30.3)	β (13.0)	β (5.1)	0.3

^a The substitution patterns were determined by a combination of mass spectral analysis of the amine fragmentation patterns by electron impact mass spectroscopy (11 eV and 70 eV) and ^2H NMR; see ref 5. Numbers in parentheses represent product as a percent of total tertiary amines recovered, usually 98%. ^b Reactions were run at 150°C for 20 h under 400 psi of CO for the metal carbonyls and 100 psi of N_2 for Pd black. Reaction solutions contained 43 mmol of amine, 0.1 mmol of metal carbonyl or 2.0 mmol Pd black, and 100 mmol of D_2O . ^c These values are (mmol amine reacted)/[(mmol catalyst)(hour)] and are the averages of at least two different runs. ^d Reaction conditions are described in ref 5. ^e Mass spectral analysis did not give a clear-cut exchange pattern. ^f Reaction time was 40 h. ^g Reaction time was 16 h.

quite similar for the homogeneous and heterogeneous catalysts, although they do change on going from Et_3N to Bu_3N , favoring α substitution and d_1 products (Table II).

With regard to the ruthenium carbonyl⁷ and Pd black catalysis⁸ of the exchange of deuterium for hydrogen, the salient features of Tables I and II are (1) the parallel changes that favor α exchange over β exchange that occur for each catalyst as the tertiary amines change from Et_3N to Pr_3N to Bu_3N , (2) the parallel changes in the patterns of exchange on going from Et_3N to Bu_3N , and (3) the parallel changes in overall exchange activity

(7) The homogeneity of the ruthenium catalyst was established by attempting to catalyze the deuterium for hydrogen exchange reaction on Et_3N using ruthenium metal powder that had been activated (caution pyrophoric) by heating at 400°C for 6 h in flowing hydrogen. We observed no catalytic activity employing conditions similar to those used for the palladium-black-catalyzed reactions.

(8) The heterogeneity of the palladium black catalyst was also tested because of the observation of unusual sintering patterns.^{9b} The heterogeneity of the palladium-catalyzed reactions was established from the fact that palladium was quantitatively recovered after the reaction. The amine solution remained colorless throughout the reaction and most importantly introduction of soluble palladium [as $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$] species in the absence of palladium black resulted in decomposition to metal and no observable catalytic reaction.

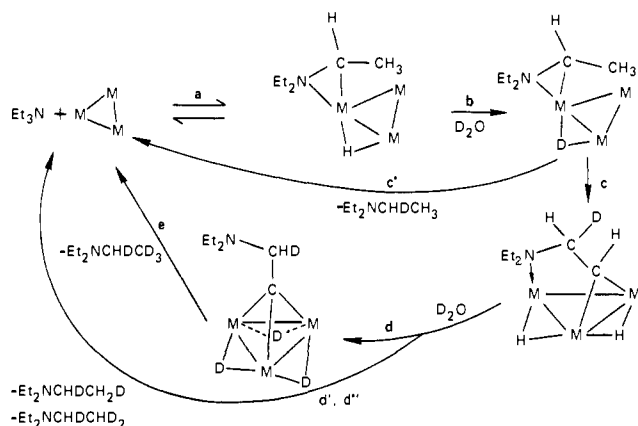


Figure 1. A possible mechanism accounting for the $\alpha\beta\beta$ deuterium for hydrogen exchange pattern catalyzed by either Pd black, $\text{Ru}_3(\text{CO})_{12}$, or $\text{Os}_3(\text{CO})_{12}$ where Et_3N is the substrate. Step c' will give $\alpha\text{-}d_1$ products. Depending on the rate of deuterium for hydrogen exchange vs. Et_3N reconstitution, d' will give $\alpha\beta\text{-}d_2$ product, d'' will give $\alpha\beta\beta\text{-}d_3$ product, and e will give $\alpha\beta\beta\beta\text{-}d_4$ product. The reverse sequence of steps may provide a route for the $\beta\beta\beta\alpha$ substitution pattern; however, our previously proposed mechanism remains viable.⁵

as the tertiary amine is varied. These changes in catalyst behavior are not purely a consequence of the increased steric bulk on going from Et_3N to Bu_3N , because catalyst activity (turnover frequency) should decrease as the alkyl groups become larger rather than increase as is observed. The anomaly lies in the Pr_3N reactions, which consistently have lower turnover frequencies and $\alpha:\beta$ ratios than would be expected from the Bu_3N results. At this point, we have insufficient information to either offer a satisfactory explanation of the changes in catalyst behavior or explain this anomaly; however, it is important to note that the anomaly is found for reactions catalyzed by both palladium black and ruthenium. One other point of interest is the fact that the ruthenium-catalyzed Et_3N exchange exhibits two different exchange pathways ($\beta\beta\beta\alpha$ and $\alpha\beta\beta\beta$). As steric hindrance increases, the $\alpha\beta\beta\beta$ exchange mechanism is favored. Figure 1 shows a plausible mechanism for the $\alpha\beta\beta\beta$ exchange.

The above observations indicate that three different catalyst-amine reaction parameters change in the same way and with much the same relative rates of change. These facts are strong support for reliable modeling. Moreover, if the modeling concept is indeed valid, it seems logical that the homogeneous catalysts should be capable of catalyzing other reactions of tertiary amines found to be catalyzed by Pd black. In this respect, we have recently reported^{9a} that reactions similar to reaction 2 (with Et_3N and Pr_3N) can be very effectively catalyzed by homogeneous catalysts deriving from $\text{Rh}_6(\text{CO})_{16}$, $\text{Ir}_4(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, and $\text{Os}_3(\text{CO})_{12}$. These results represent a fourth reaction parameter. Initial modeling studies of reaction 2 with the ruthenium catalyst have resulted in a fifth parameter. Both the ruthenium and palladium black catalysts require catalytic amounts of water for catalysis of reaction 2.^{9b}

We believe that in the homogeneous catalysis of reactions 1 and 2 the active species are clusters. Our beliefs are based on the following reasons. First, as the CO pressure is decreased, the rate of deuterium for hydrogen exchange increases rapidly for all of the active catalysts.¹⁰ Second, a bridging carbene complex similar to that formed in step c of Figure 1 has been isolated and a crystal structure obtained from the reaction of Et_3N with $\text{Os}_3(\text{CO})_{12}$.^{11,12} Third, Deeming has shown that the reactions

(9) (a) Shvo, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753. (b) Shvo, Y.; Laine, R. M., unpublished results.

(10) We have recently described criteria for identifying cluster-catalyzed reactions (Laine, R. M. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1980**, 25, 399) wherein one criterion is that the occurrence of increased catalytic activity under conditions that favor cluster formation (low CO pressures and third-row carbonyl complexes, e.g., $\text{Os}_3(\text{CO})_{12}$) is suggestive of cluster catalysis. The CO pressures used in the present studies are used solely to inhibit reaction 2.

of $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_2$ with $\text{Os}_3(\text{CO})_{12}$ produce only amine cluster complexes of osmium,¹³ and, fourth, we have isolated from reactions similar to (1) and (2) the cluster $(\eta^2\text{-CH}_3\text{C}=\text{NEt})\text{Ru}_3(\text{CO})_9\text{H}$.^{9b} Finally, we cannot describe a mononuclear catalysis mechanism for deuterium-hydrogen exchange that successfully accounts for all the observed exchange patterns.^{5,14} Unfortunately, definitive proof of cluster catalysis must await isolation of active intermediates.

The amine catalysis studies described above appear to be valuable model systems useful for delineation of the catalytic mechanism(s) of hydrodenitrogenation and may be of value in understanding the mechanisms by which amines poison catalysts.¹⁵

Acknowledgment. We thank Dr. Karl F. Kuhlmann for running the ^2H NMR MR spectra and Maria Buyco for her assistance with the manuscript. This work was supported by National Science Foundation Grant 78-25069.

(11) (a) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewyck, R. A. *J. Organomet. Chem.* **1978**, 167, C32. Note that reconstitution of Et_3N from the Shapley complex in the presence of D_2O will give either $\text{Et}_2\text{NCHDCH}_2\text{D}$ or $\text{Et}_2\text{NCHDCHD}_2$ depending on whether or not the metal hydride exchanges with D_2O . These are the only d_2 and d_3 products found with the osmium-catalyzed exchange. (b) Note also that steps c and d are similar to reactions found for $\text{HCO}_3(\text{CO})_9\text{H}_3$. Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, 99, 5225.

(12) Similar amine reactions are also reported by: Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, 19, 1795.

(13) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, 133, 123. The reaction conditions reported in this paper are more severe than those we employ.

(14) The key features that are difficult to explain with mononuclear catalysis are (1) no d_5 as $-\text{CD}_2\text{CD}_3$ is found; (2) in the rhodium reaction d_4 is $-\text{CHDCH}_2\text{D}_3$ and d_3 is always $-\text{CH}_2\text{CD}_3$, and (3) osmium is the best catalyst of all the group 8 metals at low CO pressures.

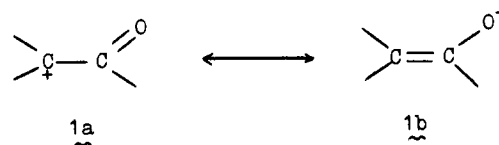
(15) These relationships will be discussed in future publications.

Stabilization of α -Keto Cations by Carbonyl Conjugation

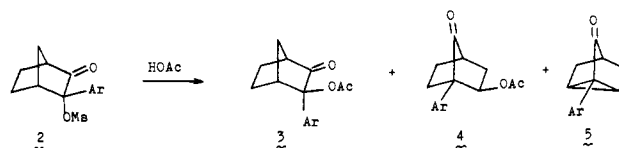
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We have previously reported that solvolytically generated α -keto cations are viable, although they are relatively unstable intermediates.¹ Evidence for this instability included their slow rate of formation, rearrangement propensity, a large $\alpha\text{-CH}_3/\alpha\text{-CD}_3$ isotope effect, and large reaction constant in a Hammett study. We now wish to report experimental evidence that the α -keto cation **1a** can derive significant stabilization by a conjugative interaction as represented by **1b**.



Acetolysis of mesylates **2** gave **3-5** in the yields shown in Table I. Increasing amounts of the rearranged acetate **4** and the tricyclic



(1) Creary, X. *J. Org. Chem.* **1979**, 44, 3938–3945.

(2) Mesylates **2** were prepared by the previously described methodology.¹ The more reactive mesylates were stable in solution but decomposed in the pure state at room temperature.