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Cesium-Induced Structural Change of Adsorbed Ethylene on Cesium-Promoted Silver Catalyst Studied by ^{13}C Solid-State Nuclear Magnetic Resonance

Jianxin Wang[†] and Paul D. Ellis*

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

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The selective oxidation of ethylene to ethylene oxide is an important industrial catalytic reaction. The reaction is performed on a Ag catalyst support on α-alumina. Alkali-metal cations are added to the catalyst in order to increase the selectivity and activity of the catalyst.[1] The further oxidation of the product, ethylene oxide, to CO_2 and H_2O, is a process which decreases the overall selectivity of the reaction, and alkali metals are known to suppress this combustion. Although the use of alkali metals is widespread in the selective oxidation of ethylene, their surface form and the mechanism of how they influence the reaction are far from clear. There have been several possible explanations of the effect of the alkali promoters. Grant and Lambert[2] proposed that since cesium cation adsorption will transfer considerable charge to the solid, much of this transferred charge is likely to reside on the electronegative oxygen, thereby making the oxygen a "softer" nucleophile. This can reduce the possibility of oxygen attacking the ethylene oxide to form acetaldehyde, which initiates the combustion reaction. However, such a postulate implies an understanding of the ion/ion-pair equilibrium at the surface. Campbell[3] suggested an ensemble-effect mechanism for the role of Cs^+ as a promoter. The assumption is that CO_2 production requires a larger number of contiguous surface sites than the ethylene oxide formation, and the high coverage of Cs^+ blocks the sites that are used for CO_2 formation. Another interpretation on the effect of Cs^+ has been put forward in the recent theoretical work by Carter and Goddard,[4] who report that an increase in selectivity upon addition of Cs^+ may be explained by Lewis acid–Lewis base interaction.

In the present work, we have investigated the effect of added Cs^+ upon the structure of the ethylene adsorbed on a 10% Ag catalyst, supported on γ-alumina. We found that the chemical shift of ethylene moves to higher shielding with increasing Cs^+ content and that the carbon–carbon bond distance of ethylene becomes longer with increasing Cs^+ content. It is apparent that Cs^+ promoters have a significant impact on the structure of ethylene on the surface of the silver.

Table I. The Bond Length and the Shielding Tensors[a,b] of Ethylene Adsorbed on a Ag Surface with Different Amounts of Cs^+ Promoter

Cs, %	0	5	10	14	18	30
$r_{C=C}$, Å	1.34	1.365	1.365	1.375	1.385	1.39
σ_{11}	190	190	191	187	193	189
σ_{22}	118	111	110	109	103	108
σ_{33}	12	10	8	6	6	4
σ_i	106.7	103.6	103.0	100.7	100.7	100.3
$\Delta\sigma$	−142	−140.5	−142.5	−142.0	−142.0	−144.5
η	0.76	0.85	0.85	0.82	0.95	0.84

[a] Chemical shifts in parts per million from external Me_4Si. [b] $\sigma_i = {}^1/_3 Tr\sigma$. $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{22} + \sigma_{11})$. $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_i)$. The absolute error for the chemical shift σ is ±2 ppm.

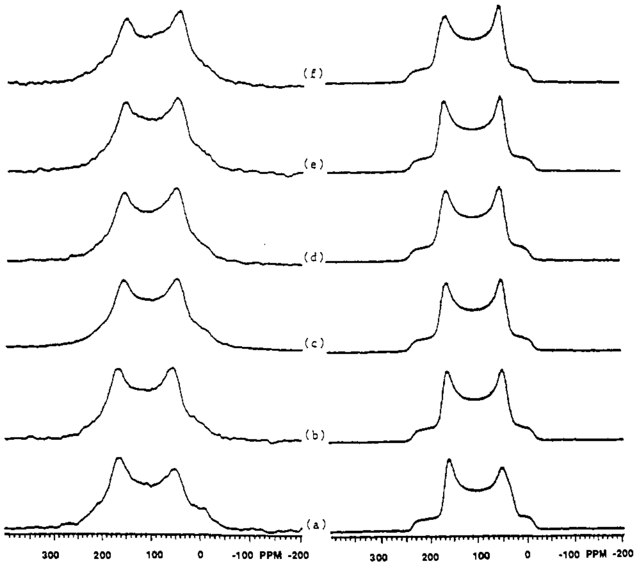

Figure 1. ^{13}C CP static spectra (75.43 MHz) of [1,2-^{13}C]ethylene adsorbed on Ag/γ-alumina with different amounts of Cs additives. On the left side are experimental results, and on the right side are the simulations. (a) No Cs additives. (b) Cs is 5%. (c) Cs is 10%. (d) Cs is 14%. (e) Cs is 18%. (f) Cs is 30%.

The samples were prepared by standard methods,[5] and the solid-state cross-polarization (CP) ^{13}C spectra were obtained on a Varian XL-300 instrument. Table I contains the principal elements of the shielding tensor along with the extracted[6] value of the $r_{C=C}$ of ethylene adsorbed on the silver catalyst surfaces for various amounts of Cs^+.[7] The shielding tensors were obtained from static spectra that were collected at 100 K. The isotropic ^{13}C chemical shift moves to higher shielding with increasing Cs^+ content. These shifts are due primarily to small changes in the value of σ_{22} and partially to changes in the value of σ_{33}. Figure 1 presents the static CP spectra of [1,2-^{13}C]ethylene on the surface of 10% Ag catalysts with different Cs^+ contents and their respective simulations. The spectra were measured at 100 K in order to quench molecular motion. The spectra clearly demonstrate a significant sensitivity of the ethylene adsorbate line shape to different amounts of added Cs^+. The bond lengths[6] increase with increasing Cs^+ content. The literature value for the C=C distance for ethylene is 1.335–1.340 Å. The carbon–carbon bond in ethylene adsorbed on the 10% Ag without the Cs^+ promoter is almost the same as that for free ethylene. This small perturbation of the bond distance reflects a weak interaction between ethylene and Ag. This is consistent with the calculations of Carter and Goddard,[4] who noted that in the absence of a positive charge the interaction between silver and ethylene was repulsive. However, when ethylene is adsorbed on the surface of a Ag catalyst with added Cs^+, theory suggests a stronger interaction and our data indicates that the structure of ethylene changes. The amount of

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[†] Union Carbide Fellow.

[1] Nielsen, R. P.; LaRochelle, J. H. Shell Oil Co. U.S. Patent 3 962 136, 1972.

[2] Grant, R. B.; Lambert, R. M. *J. Catal.* **1985**, *93*, 92.

[3] Campbell, C. T. *J. Phys. Chem.* **1985**, *89*, 5789.

[4] Carter, E. A.; Goddard, W. A., III *Surf. Sci.* **1989**, *209*, 243.

[5] Chin, Y.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 7653.

[6] Chin, Y.; Ellis, P. D., submitted to *J. Am. Chem. Soc.* Briefly, the procedure to obtain the C=C distance is as follows. Since the dipolar coupling depends on the bond distance, $r_{C=C}^{-3}$, the bond distance can be extracted by simulating the static spectrum in the presence of homonuclear dipolar interaction. Before doing the simulations, it is necessary for us to have the chemical shift tensor parameters which can be extracted from the static spectra in the absence of the homonuclear interaction, i.e., the monolabeled ethylene. The simulated spectra in Figure 1 were obtained by using the parameters in Table I.

[7] Cs and Ag were simultaneously deposited on γ-alumina, and the percentage of Cs is expressed as a total weight percent of Ag and Cs present. We outline the preparation of the surface as follows. First, silver nitrate and potassium oxalate were dissolved in the distilled water. The resulting precipitate was washed five times to remove any potassium. Second, to dissolve the precipitate, 9 mL of ethylenediamine and 0.9 mL of ethanolamine were added to the silver oxalate. This solution was then added to a solution of cesium nitrate. Five grams of γ-alumina was put into the solution and left overnight. Finally, the solution was decanted away from the γ-alumina. The surface was then dried at 120 °C for 3 h and then put into the furnace at 290 °C for 4 h to undergo calcination. The exact nature of the anion of the surface is not clear. It probably represents a mixture of carbonates and nitrates.

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change depends upon the quantity of Cs$^+$ present. The value of $r_{C=C}$ increases from 1.34 ± 0.01 Å for ethylene on the Ag catalyst with no added Cs$^+$ to 1.39 ± 0.01 Å for ethylene on 30% Cs$^+$/Ag catalyst. It is apparent that the double bond in ethylene has become weaker due to an interaction of the Cs$^+$ with the silver and/or the ethylene. Again, Carter and Goddard[4] have argued that Cs$^+$ should facilitate the binding of ethylene to the surface.

There are at least two explanations[8] for the observed changes of the chemical shift and bond length. First, it is known that electron density can be transferred from the alkali to the transition metal.[9] By such a transfer, silver is expected to become enriched in valence electron density, thereby altering its interaction with ethylene and facilitating a partial transfer of electron density to the π^* orbital of ethylene. As a result, the C=C bond distance lengthens and the carbons are more shielded, i.e., more like sp^3 carbons. Second, Cs$^+$ could be associated with the silver and the ethylene via oxygen bridges, as proposed by Carter and Goddard.[4] One can rationalize our data by a variety of hand-waving arguments. However, more experiments are necessary before one can make a clear choice. The results of selective cross-polarization and/or heteronuclear SEDOR[10] experiments will be discussed in a more detailed report on this system. It is believed that this experimental result will be helpful for the development of a model for the role of Cs$^+$ in the alkali-promoted partial oxidation of ethylene to ethylene oxide via supported Ag catalysts.

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Registry No. C_2H_6, 74-85-1; Cs$^+$, 7440-46-2; Ag, 7440-22-4.

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(8) A potential problem with these measurements is that the relative orientations of the dipole and shielding tensors could be changing as a function of the Cs$^+$ added to the surface. The line shape is relatively insensitive to small changes, i.e., ±4°, in these angles. However, if the relative orientations changed by more that ±8°, then one could not extract the bond distances from the line shapes. This possibility would require a strong (direct) interaction between the Cs$^+$ and the ethylene. The relatively small changes in the observed shielding tensor argue against this as a viable possibility. Hence, we feel that the relative orientations of the two tensors are independent (within the context of small angles) of the amount of Cs$^+$ present.

(9) Lindgren, S. Å.; Wallden, L. *Surf. Sci.* **1979**, *89*, 319.

(10) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1985**, *89*, 3606.

Stereocontrolled and Regiocontrolled Addition of Two or Three Carbon Substituents across an Arene Double Bond of Phenyloxazolines and Phenylmethanimines Coordinated to the Tricarbonylchromium Group

E. Peter Kündig,* Gérald Bernardinelli, Ronggang Liu, and Alberto Ripa

Department of Organic Chemistry, University of Geneva
1211 Geneva 4, Switzerland

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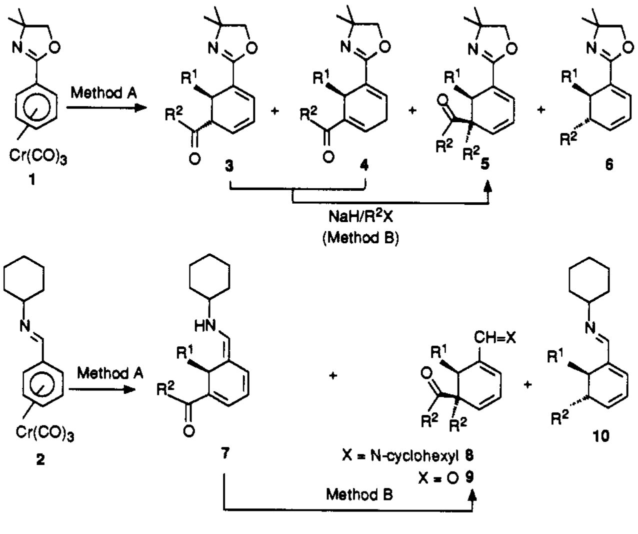
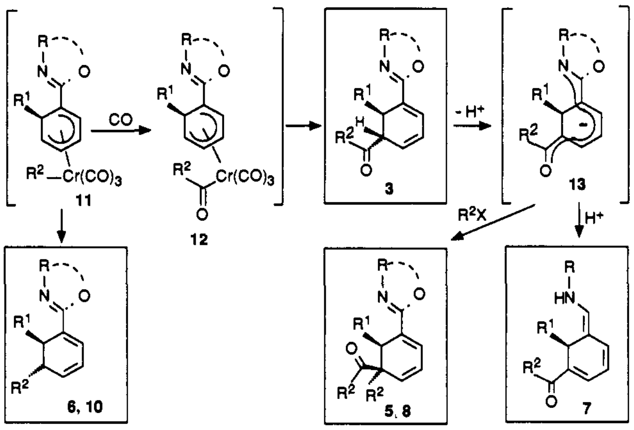
The regio- and stereocontrolled addition of substituents across an arene double bond is an attractive route to substituted alicyclic rings. Available methods are based on the activation of the arene to the first, nucleophilic, addition. Reaction of the intermediate with a carbon electrophile then introduces the second substituent.[1] Both σ-bound groups, such as oxazolines[2] and imines,[3] and the π-bound group Cr(CO)$_3$[4] activate naphthalenes[2a–e,3,4a–c] and pyridines[2f,g,4d–f,5] to the sequential nucleophile/electrophile addition, but only the Cr(CO)$_3$ group appears to be able to also activate benzene and its derivatives to the double addition. The reaction proceeds via nucleophilic addition to the exo face of the complexed arene,[6] followed by alkylation of the anionic cyclohexadienyl complex intermediate at the metal center, CO insertion, and acyl migration to the endo face of the cyclohexadienyl ligand (reductive elimination) to give, after facile metal removal, the product of a 1,2-trans alkyl/acyl addition.[7] We found that the tricarbonylchromium phenyloxazoline and phenylmethanimine complexes **1** and **2** undergo highly regioselective ortho addition of carbon nucleophiles.[8] In this paper we describe the unexpected

Scheme I



Scheme II



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(1) For examples of alternative organometallic methodologies involving a second nucleophilic addition either to a cyclohexadienyl ligand or to a carbonyl ligand, see: (a) Astruc, D. *Synlett* **1991**, *6*, 369. (b) Pike, R. D.; Sweigart, D. A. *Synlett* **1990**, *10*, 565. (c) Padda, R. S.; Sheridan, J. B.; Chaffee, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1226.

(2) (a) Meyers, A. I.; Barner, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 1865. (b) Meyers, A. I.; Hoyer, D. *Tetrahedron Lett.* **1984**, *25*, 3667. (c) Meyers, A. I.; Lutomski, K. L.; Laucher, D. *Tetrahedron* **1988**, *44*, 3107. (d) Meyers, A. I.; Roth, G. P.; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611. (e) Rawson, D. J.; Meyers, A. I. *J. Org. Chem.* **1991**, *56*, 2292. (f) Meyers, A. I.; Natale, N. R.; Wettlaufer, D. G. *Tetrahedron Lett.* **1981**, *22*, 5123. (g) Meyers, A. I.; Natale, N. R. *Heterocycles* **1982**, *18*, 13.

(3) (a) Meyers, A. I.; Brown, J. D.; Laucher, D. *Tetrahedron Lett.* **1987**, *28*, 5279. (b) Meyers, A. I.; Brown, J. D.; Laucher, D. *Tetrahedron Lett.* **1987**, *28*, 5283.

(4) (a) Kündig, E. P.; Simmons, D. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1320. (b) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (c) Kündig, E. P.; Inage, M.; Bernardinelli, G. *Organometallics* **1991**, *10*, 2921. (d) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Chem. Commun.* **1989**, 995. (e) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Chem. Commun.* **1990**, 1780. (f) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 757.

(5) With pyridines, the second step is N-alkylation or -acylation.

(6) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535.

(7) Kündig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P. *Helv. Chim. Acta* **1990**, *73*, 386.

(8) Kündig, E. P.; Amurrio, D.; Liu, R.; Ripa, A. *Synlett* **1991**, 657.

0002-7863/91/1513-9676$02.50/0