การศึกษาอิทธิพลของหมู่แทนที่ที่มีต่อการเกิดสารประกอบเชิงซ้อนซิลเวอร์(I)-โอลิฟิน โดยใช้การคำนวณออร์บิทัลเชิงโมเลกุล *Ab Initio*

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาเกี่ยวกับอิทธิพลของหมู่แทนที่ที่มีต่อการเกิดสารประกอบเชิงซ้อนระหว่างซิลเวอร์(I) และอนุพันธ์ของเอทิลลีนโดยใช้การคำนวณออร์บิทัลเชิงโมเลกุล *Ab initio* จากการศึกษาพบว่าการแทนที่ไฮโดรเจนอะตอมของเอทิลลีนด้วยหมู่แทนที่ซึ่งมีคุณสมบัติดึงอิเลคตรอนทำให้พลังงานของ π- และ π*-ออร์บิทัลของโอลิฟินลดลง ในทางตรงกันข้าม พลังงานของออร์บิทัลทั้งสองมีค่าสูงขึ้นเมื่อแทนที่ไฮโดรเจนอะตอมด้วยหมู่แทนที่ซึ่งมีคุณสมบัติให้อิเลคตรอน การเปลี่ยนระดับพลังงานของ π- และ π*-ออร์บิทัลนี้ส่งผลให้ความแตกต่างระหว่างระดับพลังงานของออร์บิทัลที่มีส่วนร่วมในการเกิดพันธะระหว่างซิลเวอร์ (I) และโอลิฟินเปลี่ยนแปลงไป รวมทั้งทำให้ความเสถียรของสารประกอบเชิงซ้อนเปลี่ยนไปด้วยเช่นกัน ความสำคัญของพันธะ σ ที่มีต่อการเกิดสารประกอบเชิงซ้อนที่เสถียรนั้นเห็นได้ชัดเจนจากการที่ความแตกต่างของพลังงานออร์บิทัลระหว่าง 5s ของซิลเวอร์และ π ของโอลิฟินมีค่าน้อยกว่าความแตกต่างระหว่าง 4d ของซิลเวอร์และ π ของโอลิฟิน นอกจากนี้ยังพบว่าค่าพลังงานยึดเหนี่ยวของสารประกอบเชิงซ้อนมีความสัมพันธ์กับความหนาแน่นของอิเลคตรอนที่มีอยู่ใน π-ออร์บิทัลของโอลิฟิน ความสอดคล้องกันระหว่างความสัมพันธ์ระหว่างค่าคงที่แฮมเมตต์กับค่าพลังงานยึดเหนี่ยวของสารประกอบและส่วนกลับของความแตกต่างระดับพลังงานระหว่าง 5s-ออร์บิทัลของซิลเวอร์และ π-ออร์บิทัลของโอลิฟินยังชี้ให้เห็นว่าหมู่แทนที่นั้นมีผลน้อยมากต่อขอบเขตของการเหลื่อมกันระหว่างออร์บิทัล ความเสถียรของสารประกอบเชิงซ้อนยังมีความสัมพันธ์กับประจุมัลลิแกนของซิลเวอร์ไอออนและการเพิ่มขึ้นของระยะทางระหว่างคาร์บอน-คาร์บอนอะตอมในพันธะคู่ของโอลิฟินด้วยเช่นกัน

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Studies of Substituent Effects on Silver(I)–olefin Complexation Using *Ab Initio* Molecular Orbital Calculations

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Abstract

The *ab* initio molecular orbital computations are performed to study the effects of substituents on the complexation between silver(1) and ethylene derivatives. It is found that substituents with electron–withdrawing ability attribute to decreases in the energies of the olefinic π– and π^*–orbitals. On the contrary, an increase of the orbital energies is observed as a hydrogen atom in ethylene is replaced by an electron–donating substituent. The changes in π– and π^*–orbital energies alters the energy difference between the appropriate orbital pairs involving in the bonding, and consequently affects the stability of the complex. The importance of the σ–bond to the formation of a stable complex is underlined by a smaller energy gap between the silver(I) 5s– and the olefinic π–orbitals relative to that of the silver(1) 4d– and the olefinic π^*–orbitals. Binding energies of the complexes are also calculated, and found to relate reasonably well to electron availability from the olefinic π–orbital. The intimate correspondence of the correlations between binding energy and the reciprocation of the energy difference between the olefinic π–orbital and the silver(1) 5s–orbital with respect to Hammett substituent constant is a clear indication that substituent has negligible effect on the overlap extent. The relative stability of the silver(1)-olefin complexes is found to relate to the mulliken charge of the complexed silver and the increase in carbon–carbon double bond distance of olefin after the complexation.

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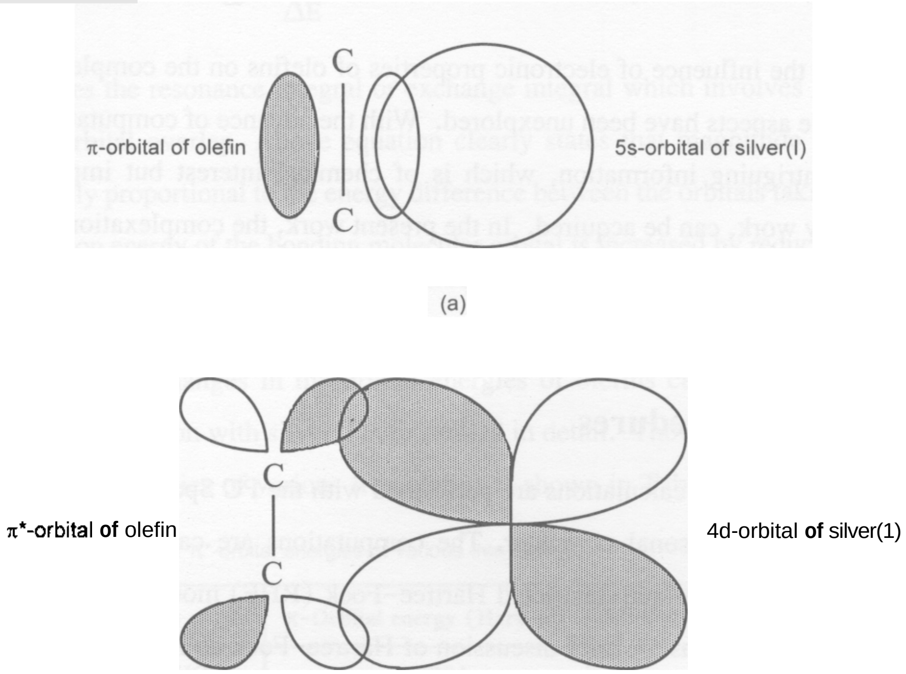
Introduction

A reversible complexation reaction between silver(1) and olefin has been used to augment the transport of olefin through facilitated transport membranes. Under conditions where the reaction is optimum, facilitated transport membrane can achieve very high separation factors of the olefins over paraffins, and high fluxes [1]. Enhancement of the membrane performance requires a profound understanding of silver(I)-olefin bonding. Despite extensive research on facilitated olefin transport using silver(I)-containing membranes, much less attention has been devoted to improving knowledge of the complexation. The present work is intended to provide some knowledge that might be needful for the membrane development.

The transition metal–olefin interaction is qualitatively elucidated by the most widely accepted model proposed by Dewar [2] and Chatt et al. [3]. According to the model, the silver(I)-olefin bonding is constituted of two synergic interactions involving o–bond and n–bond as shown in Fig. 1.



(a)

(b)

Fig. 1 Illustration **of** bonding between transition metal and olefin: (a) σ-bond; (b) π-bond

The o–bond originates from the interaction between the n–orbital of olefin and the 5s-orbital of silver(I), i.e. the electrons in the π-orbital on the olefin localize onto the empty 5s-orbital on the silver(I). An unfavorable build–up of negative charge on the silver(1) is counteracted by the x–bond, the result of the interaction between the π*-orbital of olefin and the 4d–orbital of silver(1). In this case, the electrons delocalize from the fully filled hybrid 4d–orbital on the silver(1) onto the initially empty π*-orbital (antibonding) on the olefin.

The quantitative aspects of silver(1)-ethylene bonding were provided by Basch **[4].** The electronic structure of rhe complex was calculated using nonempirical self–consistent field theory in an extended Gaussian orbital basis set. The calculation showed that the charge of the complexed silver(1) was more negative than the charge of the free silver(I), suggesting that the o–bond was stronger than the x–bond. This concept was confirmed by the orbital population analysis, which revealed that the most highly mixed molecular orbital, the HOMO of the complex, was the one made up primarily of the ethylene π–orbital.

In the previous work **[5],** ethylene, trans–1,2-dichloroethylene and their complexes with silver(1) were theoretically studied through ab initio molecular orbital calculations. The results indicated the substantial importance of the o–bond over the x–bond in the complex formation, which was in agreement with that found by Basch. Even though the previous work devoted attention to the relative importance of the bonding, it was of the opinion that the nature of olefins was also the essence of the complexation.

Although the influence of electronic properties of olefins on the complexation is notable, certain quantitative aspects have been unexplored. With the advance of computational technology, a great deal of intriguing information, which is of chemical interest but impossible to obtain through laboratory work, can be acquired. In the present work, the complexation of silver(1) with various ethylene derivatives are therefore computationally studied to fill a need of an insight into the effects of substituents on the stability of the complexes.

Computational Procedures

Ab initio SCF–MO calculations are performed with the PC Spartan Plus software version **1.5** on a Pentium MX personal computer. The computations are canied out in the geometry optimization modes with the spin–restricted Hartree–Fock (RHF) model. The 3–21G (*) basis set is used for all calculations. **A** brief discussion of Hartree–Fock ab initio model is given in the previous work **[5].**

Results and Discussion

Several ab inirio calculations of the silver(1)-olefin complexes are carried out in this study. Each olefin is derived from ethylene whose one of the hydrogen atoms is replaced with a substituent. Hammett constants of the substituents, providing a relative measure of the inductive effect, are listed in Table 1. With respect to hydrogen, the substituents with negative Hammett constants may be classified as electron–donating substituents, whereas those with the positive constants possess electron–withdrawing ability.

Substituent	Hammett constant	Substituent	Hammett constant
$-NHCH_3$	-0.30	$-H$	0.00
$-NHC_2H_5$	-0.24	$-CH_2OH$	0.08
$-C(CH_3)_3$	-0.10	$-CH_2Cl$	0.12
$-CH_2CH_3$	-0.07	$-COOCH_3$	0.32
$-CH_3$	-0.07	$-Cl$	0.37

According to frontier molecular orbital (FMO) theory, the nondegenerate orbital interaction produces two molecular orbitals, bonding and antibonding. The stabilization energy given by second-order perturbation theory relates to the energy difference between the orbitals, ΔE, as shown by equation

$$\text{Stabilization energy} = \frac{\beta}{\Delta E}$$

β denotes the resonance integral or exchange integral which involves geometrical factors and degree of orbital overlap. Above equation clearly states that magnitude of the stabilization energy is inversely proportional to the energy difference between the orbitals taking part in bonding, i.e. the stabilization energy of the bonding molecular orbital is increased by reducing the energy level separation.

Olefin	π-Orbital energy (Hartree)	X*-Orbital energy (Hartree)
$CH_2=CHNHCH_3$	-0.2903	0.2238
$CH_2=CHNHC_2H_5$	-0.2889	0.2253
$CH_2=CHC(CH_3)_3$	-0.3582	0.1940
$CH_2=CHCH_2CH_3$	-0.3599	0.1918
$CH_2=CHCH_3$	-0.3612	0.1949
$CH_2=CH_2$	-0.3797	0.1870
$CH_2=CHCH_2OH$	-0.3630	0.1831
$CH_2=CHCH_2Cl$	-0.3826	0.1630
$CH_2=CHCOOCH_3$	-0.3960	0.1170
$CH_2=CHCl$	-0.3769	0.1597

Obviously, removal of electrons from the olefinic π-orbital by an electron–withdrawing substituent results in the lower π-orbital energy. This directly affects the energy difference between the n–orbital and the silver(I) 5s–orbital. Given the higher orbital energy of the silver(I) 5s-orbital, –0.206 Hartree, the reduction in the olefinic 71–orbital energy therefore widens the energy level separation between the two orbitals as shown in Fig. 2. On the contrary, addition of electrons onto the π-orbital leads to an increase in the orbital energy and consequently narrows the'energy **gap** between the olefinic n–orbital and the 5s–orbital of silver(1).

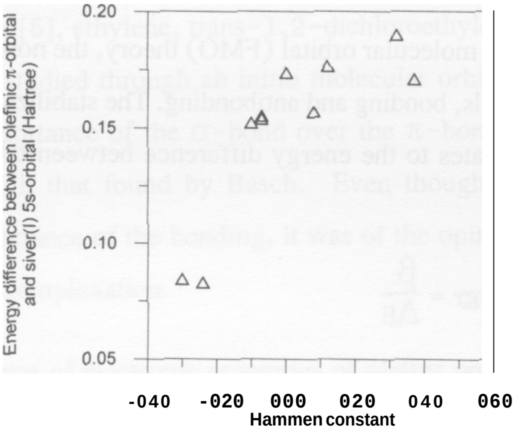


Fig. 2 Relationship between Hammett constant and the energy difference between the olefinic π-orbital and the silver(I) 5s-orbital (Hartree)

The replacement of a hydrogen atom in an ethylene by an electron–withdrawing substituent also reduces the n*–orbital energy. However, with the lower energy of the silver(1) 4d-orbita1, –0.800 Hartree, relative to the π*-orbital energy, decreasing of n*–orbital energy gives rise to the smaller energy difference. By Contrast, π*-orbital energy of the olefin increases as electron-donating ability of the substituent increases with the consequential broadening of the separation level between the olefinic π*-orbital and the 4d–orbital of silver(1). The results are presented in Fig. **3.**

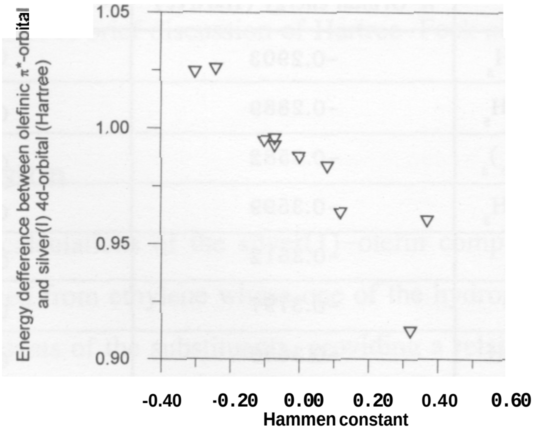


Fig. 3 Relationship between Hammett constant and the energy difference between the olefinic π*-orbital and the silver(I) 4d-orbital (Hartree)

Smaller energy gap between the olefinic π-orbital and the silver(1) 5s–orbital compared with that of the π*-orbital and the silver(1) 4d–orbital is consistent with the fact that the stabilization in the silver(1)-olefin complexation originates predominantly from the delocalization of olefinic electrons into the 5s–orbital of silver(I), i.e. 0–bonding.

By noting that the amount of energy required to dissociate the complex into free species is referred to as the binding energy or electronic dissociation energy of the complex, the binding energy is therefore a good measure of the complex stability. The relationship between the calculated binding energy, reciprocation of the energy difference between the olefinic π-orbital and the silver(1) 5s–orbital and the Hammett substituent constants are plotted in Fig. 4.

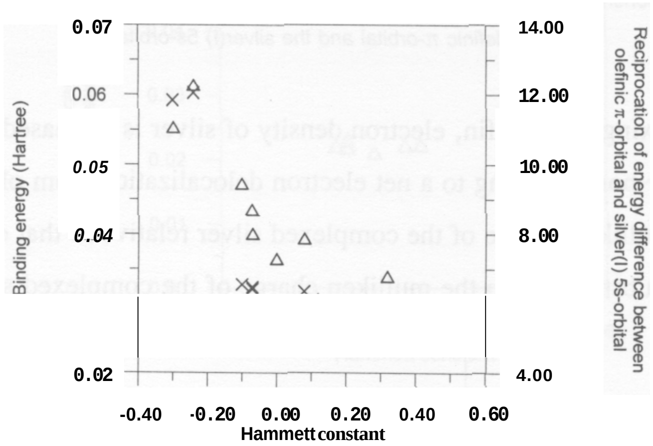


Fig. 4 Relationship between Harnrnett constant and binding energy (A), reciprocation of energy difference between the olefinic n-orbital and the silver(I) 5s-orbita(X)

With a few exceptions, binding energy of the complex and the reciprocation of the energy difference generally decrease as the electron–withdrawing ability of the substituent increases. The resemblance between these correlations presents two aspects of the complexation. First, stability of the complex is principally governed by the σ-bonding as it is evident that binding energy varies consistently to the energy difference between the orbitals taking part in the o–bond formation. This is also shown in Fig. 5. Second, in contrast to the dependence of the stabilization on the second power of the resonance integral, binding energy turns out to intimately relate to the reciprocation of the energy difference. **As** a consequence, the similarity infers that a change of substituent does not have a significant effect on the degree of the overlap.

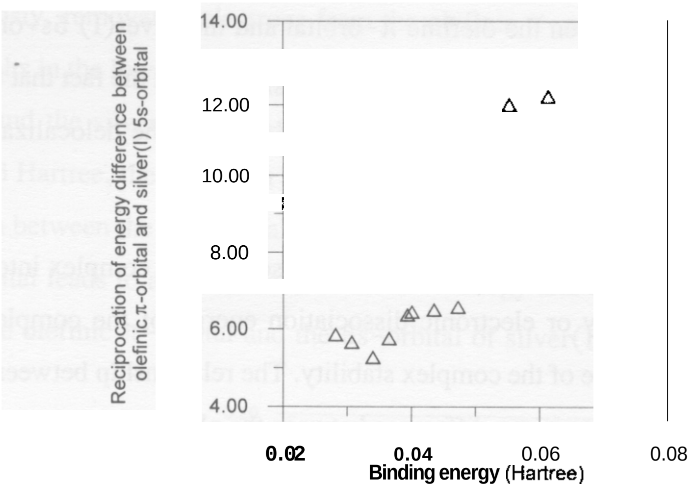


Fig. 5 Relationship between binding energy and reciprocation of energy difference between the olefinic n-orbital and the silver(I) 5s-orbital

Upon complexing with olefin, electron density of silver is increased because the 0–bond is stronger than the π-bond, leading to a net electron delocalization from olefin to silver. This is reflected in a lower mulliken charge of the complexed silver relative to that of the free ion. Fig. 6 shows the effects of substituents on the mulliken charge of the complexed silver.

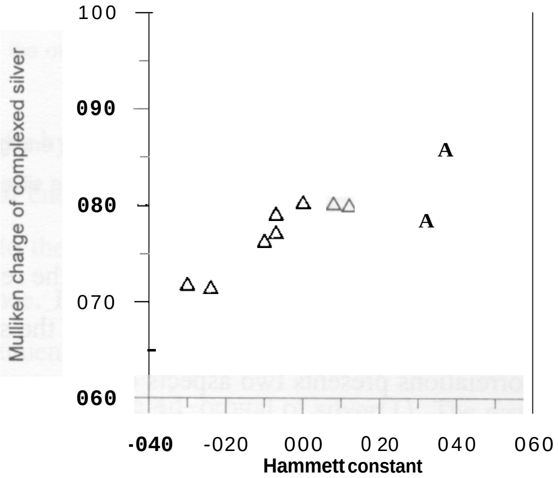


Fig. 6 Relationship between Hammett constant and mulliken charge of the complexed silver

The mulliken charge of the complexed silver, for the most part, decreases as the Hammett constant decreases. Apparently, an increase in the electron density of the olefinic 71–orbital allows more electrons to delocalize onto the silver(1) 5s–orbital. This results in a strengthened σ-bond, the essence of the complex formation, and is clearly demonstrated by the corresponding increase in the binding energy as previously discussed.

The increase in the carbon–carbon double bond distance of olefin upon complexation with silver(1) is a well known phenomenon. This increase is due to the loss of the olefinic π–electrons to the silver(1)-olefin σ–bond which results in the weakening of the carbon–carbon double bond characteristic. The increase in the carbon–carbon double bond length therefore indicates the effectiveness in electron delocalization from olefins to silver(1). The longer carbon–carbon double bond distance of the complexed olefin compared with that of uncomplexed olefin is also observed in this study, **as** shown in Fig. 7.

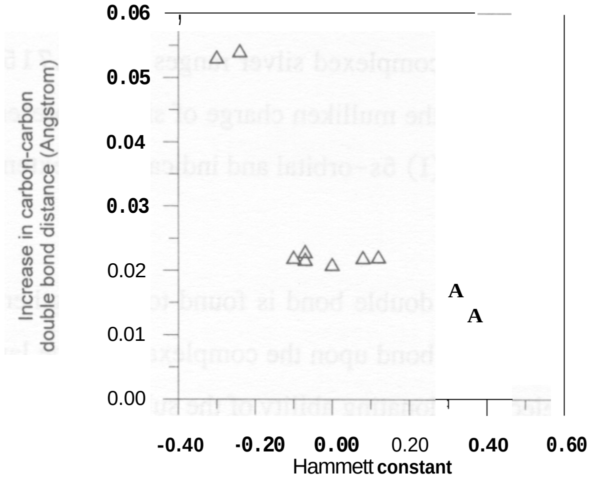


Fig. **7** Relationship between Hammett constant and increase in olefinic carbon-carbon double bond distance

The increase in the carbon–carbon double bond distance in going from free olefin to the complex justifiably correlates with the Hammett constant. This is consistent with the fact that the electron donating substituent contributes to a relatively strong interaction between silver(1) and olefin and, correspondingly, a large increase in the double bond length.

Conclusions

The formation of the silver(1)-olefin complexes are simulated by an ab initio geometry optimization at the Hartree–Fock 3–21G (*) level of theory. By replacing a hydrogen atom in ethylene with substituents having a wide range of Hammett constants, –0.3 to 0.37, an in–depth study of the influence of the olefinic n–electron availability on the complex formation are achieved. Molecular orbital analysis reveals that the energy difference between the silver(1) 5s–orbital and the olefinic n–orbital decreases as electron density in the n–orbital increases. On the other hand, reduction in the availability of the n–orbital causes the energy level separation between the silver(1) 4d–orbital and the olefinic n*–orbital to decrease.

The energy difference between the orbitals taking part in the σ-bonding, ranging from 0.0843–0.171 Hartree, is smaller than that of the 71–bonding by approximately 0.722–0.942 Hartree. Based upon frontier molecular orbital (FMO) theory, this points to the dominance of the 0–bonding in the complexation. The concept is corroborated by a relationship between the binding energy and the reciprocation of the energy gap between the silver(1) 5s–orbital and the olefinic π-orbital. In addition, the similarity of the correlations relative to the Hammett constant also suggests that the substituent does not significantly affect the shape of the 71–orbital, and, as a result, the overlap extent between the orbitals participating in the 0–bonding.

The mulliken charge of the complexed silver ranges from 0.715 to 0.858, compared to 1 for the free ion. The reduction in the mulliken charge of silver represents the electron donation of the olefinic π-orbital to the silver(1) 5s–orbital and indicates the extent of the silver–oletin σ-bonding.

The olefinic carbon–carbon double bond is found to be lengthened by 0.0107–0.0532 Angstrom due to a weakening of the bond upon the complexation. The larger increase of the bond distance is observed as the electron–donating ability of the substituents increases. This implies that a relatively more stable complex is formed when the olefin possesses greater 71–electrons availability.

Acknowledgment

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References

1. Way, J.D., and Noble, R.D., 1992, “Chapter 44–Facilitated Transport” in Membrane **Handbook,** Ho, W.S., Sirkar, K.K., Eds.: New York: Van Nostrand Reinhold, 833.
2. Dewar, M.J.S., 1951, “A Review of the 71–Complex Theory,” Bulletin de la Societe Chimique de France, Vol. 18, C71–9.
3. Chatt, J., and Duncanson, L.A., 1953, “Olefin Co–ordination Compounds. Part Ⅲ Infrared Spectra and Structure: Attempted Preparation of Acetylene Complexes,” Journal of the Chemical Society (London), 2939.

Bash, **H.,** 1972, “Electronic Structure of the Silver (l+)-Ethylene Complex,” Journal of Chemical Physics, Vol. 56, 441.

Sungpet, **A.,** 1997, “Chapter 3–Conceptual Studies of Olefin-silver(1) Ion Complex Formation” in Reactive Polymer Membranes for Olefin Separations, Ph.D. Thesis, Colorado School of Mines, 21.

Dean, **J.A.,** 1987, Handbook of Organic Chemistry, McGraw–Hill, New **York.**