2. H. S. Yu, W. J. Choi, K. T. Lim, and S. K. Choi, *Macromolecules*, **21**, 2894 (1988).
3. W. J. Choi, Y. B. Kim, S. K. Kwon, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, accepted (1992).
4. (a) C. D. Deported, L. N. Venkateshwaran, G. A. York, G. L. Wilkes, and J. E. McGrath, *Polym. Prepr.*, **30**(1), 201 (1989); (b) A. Hirao, H. Kato, K. Yamaguchi, and S. Nakahama, *Macromolecules*, **19**, 1294 (1986).
5. J. P. Hautekeer, S. K. Varshney, R. Fayt, C. Jacobs, R. Jerome, and Ph. Teyssie, *Macromolecules*, **23**, 3893 (1990).
6. (a) T. Ishizone, A. Hirao, and S. Nakahama, *Macromolecules*, **22**, 2895 (1989); (b) K. Suzuki, K. Yamaguchi, A. Hirao, and S. Nakahama, *Macromolecules*, **22**, 2607 (1989); (c) C. D. Deporter, T. E. Long, L. N. venkateshwaren, G. L. Wilkers, and J. E. McGrath, *Polym. Prepr.*, **29**(1), 343 (1988).
7. S. Kanaoka, M. Minoda, M. Sawamoto, and T. Higashimura, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 1127 (1990).
8. M. Minoda, M. Sawamoto, and T. Higashimura, *Macromolecules*, **20**, 2045 (1987).
9. T. E. Long, A. D. Broske, D. J. Bradley, and J. E. McGrath, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 4001 (1989).
10. J. J. Maurer, D. J. Eustace, and C. T. Ratcliffe, *Macromolecules*, **20**, 196 (1987).
11. N. A. Doherty, F. Gores, P. M. Mai, and A. H. E. Müller, *Polym. Prepr.*, **29**(2), 73 (1988).
12. T. E. Long, R. D. Allen, and J. E. McGrath, *Polym. Prepr.*, **27**(2), 54 (1986).

Electron-Impact Ionization Mass Spectroscopic Studies of Acetylene and Mixed Acetylene-Ammonia Clusters as a Structure Probe

Sung-Seen Choi, Kwang Woo Jung, and Kyung-Hoon Jung*

Center for Molecular Science and Department of Chemistry,
Korea Advanced Institute of Science and Technology, Taejon 305-701

Received February 27, 1992

Ion-molecule reactions of acetylene and mixed acetylene-ammonia cluster ions are studied using an electron impact time-of-flight mass spectrometer. The present results clearly demonstrate that $(C_2H_2)_n^+$ cluster ion distribution represents a distinct magic number of $n=3$. The mass spectroscopic evidence for the enhanced structural stabilities of $[C_6H_4 \cdot (NH_3)_m]^+$ ($m=0$-8) ions is also found along with the detection of mixed cluster $[(C_2H_2)_n \cdot (NH_3)_m]^+$ ions, which gives insight into the feasible structure of solvated ions. This is rationalized on the basis of the structural stability for acetylene clusters and the dissociation dynamics of the complex ion under the presence of solvent molecules.

Introduction

In recent years, the so-called intracluster ion-molecule reactions[1-9] have become a subject of great interest in the cluster ion chemistry due to its unique position between bimolecular gas-phase reaction dynamics and ionic solution chemistry. The study of a specific chemical reaction within a cluster ion is especially interesting since it is possible to directly observe how chemical reactivity changes as a function of stepwise solvation by simple monitoring the changes in reaction channel versus the cluster size.[10] A considerable amount of experimental and theoretical attention[11] has been also given to cluster systems in which small number of solvent molecules are bound to a solute molecule. The investigation of solvent effects provides knowledge of the mechanisms of "internal ion-molecule reaction" in clusters, giving direct information on the influence of solvation and insight into the structure of solvated ions.

It has been known that for small hydrogen-bonded cluster ions the stabilities of mixed cluster ions, based on the thermochemical data[12] and relative cluster ion intensity studies,[13] can be often well correlated to the complete solvation shell structures with chain-like hydrogen-bonding such as for $(NH_3)_4 \cdot NH_4^+$, $(H_2O)_4 \cdot ((CH_3)_3N)_6H^+$, and $(CH_3OCH_3)_3 \cdot H_3O^+$. This intriguing result makes it possible to investigate how the nature of a solvating component may affect the subsequent dissociation reaction and the stability of mixed cluster ion.

The acetylene clusters have been widely studied by the molecular beam mass spectroscopy incorporating VUV photoionization[14,15] and electron-impact ionization.[16] Recently, Shinohara *et al.*[17] have found the unprotonated acetylene cluster ions, $(C_2H_2)_n^+$ ($n=2$-4), using the near-threshold photoionization method, showing that these ions are produced from the mixed cluster ions followed by loss of the argon or helium used as a carrier gas through evaporation process. For unprotonated acetylene cluster ions, however, very little information is known about the pronounced magic number and whether or not "stable structures" exist in the binary system containing polar solvent molecules.

In this paper, we report an electron impact ionization of acetylene clusters and acetylene/ammonia heteroclusters. In

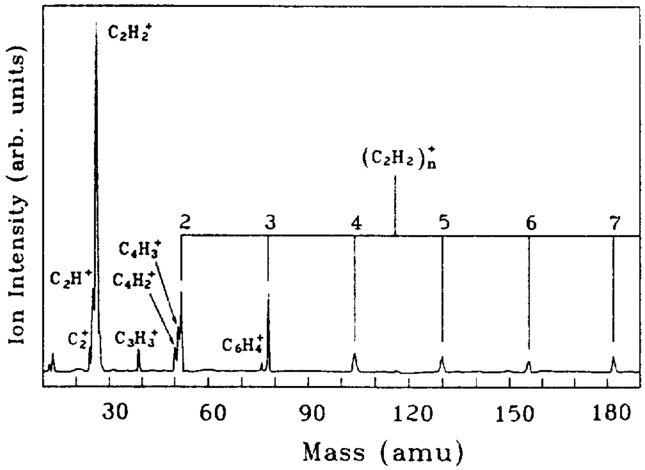

Figure 1. The electron impact TOF mass spectrum of 3% acetylene in 64 psi He (70 eV).

addition to observing a magic number of $n=3$ in the $(C_2H_2)_n^+$ cluster ion distribution, we have found mass spectroscopic evidence for the existence of enhanced structural stabilities at the $[C_6H_4\cdot(NH_3)_m]^+$ ($m=0$-8) ions along with the detection of heterocluster ions $[(C_2H_2)_n\cdot(NH_3)_m]^+$, which gives insight into the feasible structure of solvated ions. This dynamical process occurring within the ionized acetylene/ammonia heterocluster is interpreted within the framework of the structural stability and dissociation mechanism for the acetylene clusters under the presence of ammonia solvation. The variatiion of acetylene/ammonia intracluster ion-molecule reaction as a function of electron impact energy, mixing ratio, and expansion condition is also reported.

Experimental

The details of the experimental apparatus have been described elsewhere.[18] In brief, the acetylene and acetylene/ammonia mixed clusters are generated in a supersonic expansion through a pulsed nozzle at total pressure up to 64 psi with He as a carrier gas. After skimming by a conical skimmer (800 μm diameter) and collimated, the cluster beam is introduced into the ionization region of a time-of-flight mass spectrometer (TOFMS) where a pulsed electron beam intersects it at orthogonal direction. A channel electron multiplier (Murata, EMS-2082B) is used to record time-of-flight mass spectra of the cluster ions and the signal is then amplified by a preamplifier. The amplified signal is fed directly into a 175 MHz transient digitizer coupled to an IBM PC/AT computer. The experiments operate at 2 Hz and typically TOF spectra are accumulated for 500 pulses.

The acetylene and ammonia were obtained from Matheson with a quoted purity of 99.6% and 99.99%, respectively. Gas sample was used without further purification, except for acetylene, which was passed through a dry ice/acetone trap to remove acetone, normally used as a stabilizer, from the acetylene cylinder.

Results and Discussion

Pure Acetylene System. Figure 1 shows the TOF mass spectrum of a pulsed molecular beam expanded from 64 psi He containing 3% acetylene at 70 eV impact energy. The dominant cluster ions in the mass spectrum consist of a series of the unprotonated cluster ions $(C_2H_2)_n^+$ which have never been observed by electron impact ionization of acetylene clusters.[16] A very similar result has been recently reported in the near-threshold vacuum UV photoionization of the acetylene clusters seeded in Ar and He at a stagnation pressure as high as 73 psi.[17]

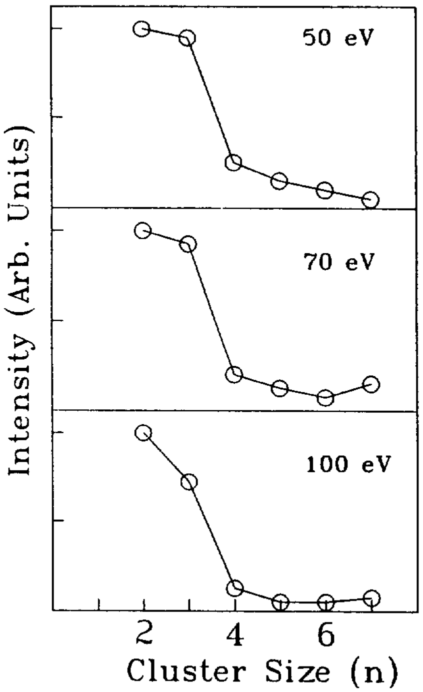

Figure 2. Plot of the cluster ion intensities as a function of acetylene cluster size n. Acetylene (3%) was seeded in 64 psi He. Ion intensities are normalized to the cluster ion with $n=2$.

The ion-molecule reaction of acetylene have been the subject of numerous investigations over the years.[14] These studies show that $C_4H_3^+$ and $C_4H_2^+$ are the major product ions when $C_2H_2^+$ reactant ion is formed by electron impact ionization or photoionization:

$$C_2H_2^+ + C_2H_2 \longrightarrow C_4H_3^+ + H \quad (1)$$

$$\longrightarrow C_4H_2^+ + H_2 \quad (2)$$

$$\longrightarrow C_2H_3^+ + C_2H \quad (3)$$

In Figure 1, the observation of the fragmented ions $C_4H_3^+$ $C_4H_2^+$, $C_2H_3^+$, and their cluster homologues is consistent with the conventional ion-molecule reactions (1)-(3). The origin of the fragment ion $C_3H_3^+$, however, is somewhat different. The $C_3H_3^+$ ion is not produced by the above ion-molecule reaction. In a recent study, Shinohara and co-workers[17] found that the intensities of the $C_3H_3^+$ and $(C_2H_2)_3^+$ ions exhibit the same pressure dependence, which suggests that the $C_3H_3^+$ ions is produced by decomposition of $(C_2H_2)_3^+$. Furthermore, the $C_3H_3^+$ ion is shown to be one of the major fragment ions in the multiphoton ionization fragmentation of benzene.[19-21] Interestingly, the peak due to an $C_6H_4^+$ ion is also observed in the spectrum. It should be noted here that the $C_6H_4^+$ ion intensity is much clearer when the electron impact energy

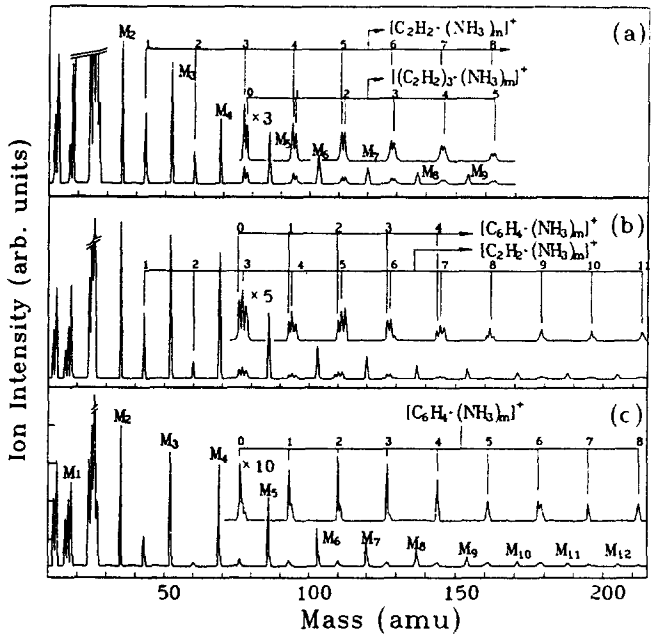

Figure 3. Comparison of electron impact (70 eV) TOF mass spectra of acetylene and ammonia mixed clusters seeded in 64 psi He. The mixing ratios are (a) 4% C_2H_2/0.3% NH_3, (b) 4% C_2H_2/0.6% NH_3, and (c) 4% C_2H_2/1.0% NH_3, respectively. M_m designates the $(NH_3)_mH^+$ cluster ion.

is increased. This fragmented ion is produced as a result of the dissociation process from acetylene trimer ion under the high excitation energy[15] and will be discussed thoroughly in the following section.

In addition to the expected fragment peaks, mass spectrum in Figure 1 is composed of a sequence of cluster ions with the formula $(C_2H_2)_n^+$ which one could naturally attribute to the unreacted parent cluster ion, *i.e.*, no protonation reaction. Figure 2 summarizes the results of normalized cluster ion intensities, $(C_2H_2)_n^+$, as a function of acetylene cluster size n which are obtained at three different electron impact energies. A distinct feature is readily discerned from the plot: there exists the salient intensity break between $n=3$ and 4 in otherwise monotonic decrease of the cluster distributions, although the discontinuity exhibits a propensity of decrease at high electron energy of 100 eV due to an evaporative mechanism caused by the deposition of excess energy within cluster ions. This evidence is suggestive of the fact that acetylene trimer ion exhibits a pronounced magic number, thereby having the stable geometry. This is in contrast to the ethylene cluster[8] where a pronounced magic number, $n=4$, cannot be explained solely in terms of stabilities of either the neutral or ionic parent ethylene clusters. Ono and Ng[15] have discussed the energetics and dissociation dynamics of the complex ion such as $C_6H_6^+$ from $(C_2H_2)_3^+$. Their studies indicate that the most probable structure of the $(C_2H_2)_3^+$ ion is that of the benzene ion $C_6H_6^+$ which obviously has a particular stability. From the observation of intensity drop between $(C_2H_2)_3^+$ and $(C_2H_2)_4^+$ in this study, it appears logical that the thermodynamic stabilities of the acetylene trimer ion is the controlling factor.

Mixed Acetylene/Ammonia System. In order to understand the effects of solvation by a polar solvent, solute-solvent clusters are generated in supersonic molecular beams, typically by coexpanding a mixture of the chromophore, solvent molecules and buffer gas through a small orifice into vacuum. Figure 3 exhibits the electron impact ionization TOF mass spectra of the acetylene and ammonia mixed clusters seeded in 64 psi helium at different mixing ratios. One may immediately notice that the overall spectral pattern looks quite different from that of the pure acetylene clusters in helium as shown in Figure 1. Despite of the trace amount of ammonia a major sequence of ion peaks, $(NH_3)_mH^+$ (designated as M_m in the mass spectra), is observed which closely resembles the mass spectrum of a pure ammonia seeded in He expansion under the same conditions. This is consistent with the view that ammonia clusters of various sizes are easily formed in a supersonic expansions as compared with the so-called van der Waals clusters such as acetylene due to its feasible hydrogen bonding.

Apart from the observation of ammonia homocluster ions, a surprising number of heterocluster ion species of the type $[C_2H_2\cdot(NH_3)_m]^+$ ($m=0$-11) and $[(C_2H_2)_3\cdot(NH_3)_m]^+$ ($m=0$-5) are also observed in the mass spectra of Figures 3(a) and 3(b). The $[(C_2H_2)\cdot(NH_3)_m]^+$ cluster ions, however, cannot be identified because its mass spectrum is coincide with the mass peaks of $(NH_3)_mH^+$ ($m\geq3$). The unprecedented detection of these heterocluster ions is attributed to the solvation of ammonia molecules around the acetylene monomer and trimer ions through hydrogen bonding. Although the $[(C_2H_2)_n\cdot(NH_3)_mH^+]$ cluster ions may be formed under the electron impact ionization, its contributions are less probable, as illustrated in the mass spectra, due to the weak van der Waals force between the acetylene molecule and the hydrogen atoms bonded to ammonia.

As the mixing ratio of acetylene/ammonia is decreased, a number of very interesting phenomena are seen in the mass spectra of these heteroclusters. One observes an overall decrease in the intensities of the heterocluster ions relative to the homocluster ions as illustrated in Figure 3. Moreover, new sequence of heterocluster ions of the type $[C_6H_4\cdot(NH_3)_m]^+$ ($m=0$-8) now emerges throughout the observed mass spectrum. At the higher concentration of ammonia greater than 1.0%, major peaks of heterocluster ions are consist of $[C_6H_4\cdot(NH_3)_m]^+$ cluster ions only. The dominant $[C_6H_4\cdot(NH_3)_m]^+$ cluster ion at the high concentration of ammonia is rather puzzling. According to the previous studies by Ono and Ng[15], under the condition of high excitation energy $(C_2H_2)_3^+$ ion dissociates to produce the fragment ion $C_6H_4^+$ having the benzyne structure:

$$(C_2H_2)_3^+ \longrightarrow (C_6H_4^+)^* \longrightarrow C_6H_6^+ + H_2 \qquad (4)$$

where $(C_6H_6^+)^*$ signifies intact complex ion with a high energy content. This dehydrogenation is also reported recently in the reaction of metal ion with benzeene by Zakin *et al.*[22]

As Figure 3 shows, the striking reduction in the intensities of the heterocluster ions relative to the homocluster ions can be interpreted as the less efficient heterocluster formation under the condition of relatively large amount of polar solvent molecules. One of the possible rationales of our result is, therefore, that the excess energy dissipation of $(C_2H_2)_3^+$ ion surrounded by the ammonia molecules is much

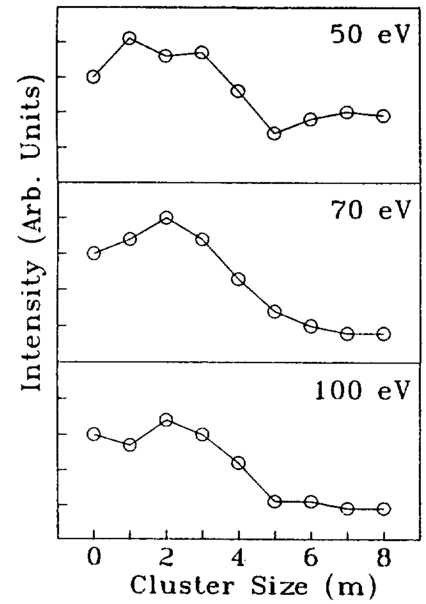

Figure 4. Plot of the $[C_6H_4\cdot(NH_3)_m]^+$ ion intensities as a function of ammonia cluster number m at different electron impact energies. Acetylene (4%) and ammonia (1.0%) were seeded in 64 psi He. Ion intensities are normalized to the cluster ion with $m=0$.

less effective in the low acetylene/ammonia mixing ratios, so that the acetylene trimer ion is presumably subjected to dissociation. That is, the large excess imparted to the complex ions, $[(C_6H_6^+)^*\cdot(NH_3)_m]$, primarily induce the cleavage of the C-H bonds in the benzene-like moiety as well as the breakup of the weak van der Waals bonds of solvent molecules in the complex. In a different set of experiments, we have measured the stagnation pressure dependence on the ion in intensities of heterocluster ions and found that even at the high mixing ratio (4% C_2H_2 and 0.3% NH_3), $[C_6H_4\cdot(NH_3)_m]^+$ ions also appear as the stagnation pressure is reduced. This result demonstrates that excess energy cannot be effectively dissipated through solvent evaporation at lower expansion condition. Furthermore, it is tempting to consider that solvation of ammonia molecules around the $C_6H_4^+$ ion can play significant role in the stable structure formation of core ion, as compared with the results from pure acetylene in He system.

Further information on this heterocluster ions comes from a comparison of relative ion intensities. In order to assure the structure of $C_6H_4^+$ ion, the intensity distributions of the heterocluster ions $[C_6H_4\cdot(NH_3)_m]^+$ ($m=0$-8) are plotted as a function of m in Figure 4. The present observation might support the benzyne structure, in that there is intensity discontinuity between $[C_6H_4\cdot(NH_3)_4]^+$ and $[C_6H_4\cdot(NH_3)_5]^+$ ions especially at 50 eV energy, indicating a special stability of the benzyne ion in an ammonia solvation. The assigned magic number is further confirmed at different mixing ratios of the two components (acetylene/ammonia = 13/1-1/2), electron impact energies (50-100 eV) and expansion conditions (44-64 psi), showing that this notable feature does indeed result from the bonding characteristics of the cluster ions and not from a particular set of experimental conditions chosen for the investigation.

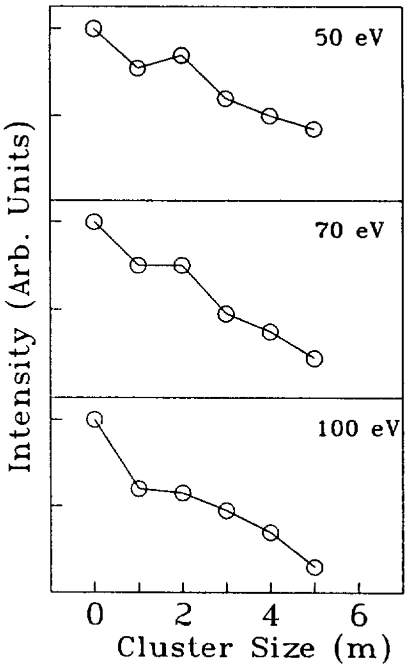

Figure 5. Plot of the $[(C_2H_2)_3\cdot(NH_3)_m]^+$ ion intensities as a function of ammonia cluster number m at different electron impact energies. Acetylene (4%) and ammonia (0.3%) were seeded in 64 psi He. Ion intensities are normalized to the cluster ion with $m=0$.

In a recent study, Craw *et al.*[23] reported the coupled Hartree-Fock calculations in which the geometrical configuration of neutral acetylene trimer has a cyclic C_{3h} structure as the global minimum. To the extent that cyclic C_{3h} structure is expected for the acetylene trimer ion, the available hydrogen-bonding sites will be three if there exist the solvent molecules such as ammonia. We can now speculate as to whether the acetylene trimer ion represents an above structure or not. The intensity distributions of the $[(C_2H_2)_3\cdot(NH_3)_m]^+$ ions ($m=0$-5) are plotted as a function of m at three different electron impact energies in Figure 5. Certainly, there is no clear break down in the intensity distribution between $m=3$ and 4, indicating that the acetylene trimer ion does not definitely afford a cyclic C_{3h} geometry. From the results given here, the most probable structure of $(C_2H_2)_3^+$ ion can be predicted as the benzene structure of acetylene trimer ion is thus feasible.

In conclusion, it is becoming increasingly evident that the study of magic numbers in heterocluster ions reveals the presence of especially stable structures. The present results provide direct evidence for the formation of stable cyclic structures at particular cluster sizes under the circumstances of polar solvent molecules. The study of the appearance of enhanced stable ions rearranged from some van der Waals culster ion is of extreme interest and importance. Such investigations are now in progress.

Acknowledgement. This work was carried out with financial assistance from the Korea Standards Research Institute and the Korea Science & Engineering Foundation, which is gratefully acknowledged.

References

1. A. J. Stace and C. Moore, *J. Am. Chem. Soc.*, **105**, 1814 (1983).
2. H. Shinohara, N. Nishi, and N. Washida, *J. Chem. Phys.*, **84**, 5561 (1986).
3. K. E. Schriver, A. M. Camarena, M. Y. Hahn, A. J. Paguia, and R. L. Whetten, *J. Phys. Chem.*, **91**, 1786 (1987).
4. J. F. Garvey and R. B. Bernstein, *Chem. Phys. Lett.*, **143**, 13 (1988).
5. H. Shinohara, N. Nishi, and N. Washida, *Chem. Phys. Lett.*, **153**, 417 (1988).
6. H. Shiromaru, H. Suzuki, H. Sato, S. Nagaoka, and K. Kimura, *J. Phys. Chem.*, **93**, 1832 (1989).
7. S. Morgan and A. W. Castleman, Jr., *J. Phys. Chem.*, **93**, 4544 (1989).
8. M. T. Coolbaugh, W. R. Peifer, and J. F. Garvey, *Chem. Phys. Lett.*, **168**, 337 (1990).
9. S. Wei, Z. Shi, and A. W. Castleman, Jr., *J. Chem. Phys.*, **94**, 3268 (1991).
10. J. F. Garvey, W. R. Peifer, and M. T. Coolbaugh, *Acc. Chem. Res.*, **24**, 48 (1991).
11. J. J. Breen, K. Kilgore, W. -B. Tzeng, S. Wei, R. G. Keese, and A. W. Castleman, Jr., *J. Chem. Phys.*, **90**, 11 (1989).
12. Y. K. Lau, P. S. Saluja, and P. Kebarle, *J. Am. Chem. Soc.*, **102**, 7429 (1980).
13. A. J. Stace and C. J. Moore, *J. Phys. Chem.*, **86**, 3681 (1982).
14. Y. Ono and C. Y. Ng, *J. Chem. Phys.*, 77, 2947 (1982); see also references cited therein.
15. Y. Ono and C. Y. Ng, *J. Am. Chem. Soc.*, **104**, 4752 (1982).
16. G. Fischer, R. E. Miller, P. F. Vohralik, and R. O. Watts, *J. Chem. Phys.*, **83**, 1471 (1985).
17. H. Shinohara, H. Sato, and N. Washida, *J. Phys. Chem.*, **94**, 6718 (1990).
18. K. W. Jung, S. S. Choi, and K. -H. Jung, *Rev. Sci. Instrum.*, **62**, 2125 (1991).
19. L. Zandee and R. B. Bernstein, *J. Chem. Phys.*, **71**, 1359 (1979).
20. U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, **72**, 4327 (1980).
21. J. P. Reilly and K. L. Kampa, *J. Chem. Phys.*, **73**, 5468 (1980).
22. M. R. Zakin, R. O. Brickman, D. M. Cox, and A. Kaldor, *J. Chem. Phys.*, **88**, 5943 (1988).
23. J. S. Craw and M. A. C. Nascimento, *Chem. Phys. Lett.*, **172**, 265 (1990).

Disappearance of the α-Effect: Reaction of p-Nitrophenyl Acetate with Various Aryloxides and Benzohydroxamates in the Presence of Cetyltrimethylammonium Bromide

Dong-Sook Kwon, Seung-Eun Lee, Jin-Kyung Jung, Jong-Yoon Park†, and Ik-Hwan Um*

Department of Chemistry, and †Department of Science Education, Ewha Womans University, Seoul 120-750. *Received March 4, 1992*

The rate constants for the reactions of *p*-nitrophenyl acetate with 6 different aryloxides and 2 benzohydroxamates have been measured spectrophotometrically in water containing various concentrations of cetyltrimethylammonium bromide (CTAB). The reactivity of the nucleophiles has been demonstrated to be significantly enhanced as the concentration of the surfactant increases up to a certain point. When the basicities of the aryloxides are comparable, the rate enhancement is more prominent for the aryloxide having larger binding constant to the micellar aggregate. Benzohydroxamates exhibitis significantly large α-effect in the absence of the surfactant, although, the α-effect nucleophiles are considered to be more solvated in water than the corresponding normal nucleophile. Thus, the solvation effect does not appear to be solely responsible for the α-effect. Interestingly, the large α-effect disappears in the presence of the surfactant. Therefore, one might attribute the disappearance of the α-effect to solvent effect. However, a structural change of the reactive α-effect nucleophile into unreactive ones would also be considered to be responsible for the absence of the α-effect in the present system.

Introduction

Rationalization of nucleophilicity has intrigued organic chemists for some decades and numerous factors have been suggested to be important for correlation of nucleophilic reactivity.[1-3] Among them, the basicity of nucleophiles has most successfully been used as a measure of nucleophilicity.[3] However, a group of nucleophiles containing a hetero atom in the α-position from the reaction center has exhibited abnormally higher nucleophilicity than would be expected from their respective basicity. Thus, the enhanced reactivity of these nucleophiles has been termed the α-effect.[4] The origin of the α-effect has not been well understood.[5] Particularly, the theory concerning solvent effect has been contradictory, *i.e.*, some studies have claimed solvent effect is unimportant for the α-effect[6] but other studies have suggested that solvation should be an important factor.[7]

Recently a series of systematic studies has revealed that