layer (3 cm) of Al_2O_3. The solution was concentrated to 2 mL and hexane (20 mL) was added to precipitate the product as an orange-red air-stable solid. Yield 38 mg (47 %). ^1H NMR (400.13 MHz, [D_1]chloroform, 25 °C): $\delta = -0.69$ (bs, 2H; cage CH), 1.60 (s, 15H; C_5Me_5), 5.22 ppm (s, 5H; C_5H_5); $^{11}B\{^1H\}$ NMR (128.38 MHz, [D_1]chloroform, 25 °C): $\delta = -5.26$ (2B), 16.24 (2B), 17.92 (2B), 31.94 (1B), 38.31 (1B), 95.10 ppm (1B); elemental analysis (%) calcd: C 38.17, H 5.84, B 18.19; found: C 38.16, H 5.89, B 18.11.

[(η-C_5Me_5)Ru($C_2B_9H_{11}$)Ru(η-C_5Me_5)] (**2b**): THF (4 mL) was added to a mixture of [{(η-C_5Me_5)RuCl}$_4$] (41 mg, 0.038 mmol) and Tl-**1** (86 mg, 0.15 mmol). The reaction mixture was stirred for 4 h and filtered through a thin layer (3 cm) of Al_2O_3. The solution was concentrated to 2 mL and hexane (20 mL) was added to precipitate the product as a red air-stable solid. Yield 67 mg (74 %). ^1H NMR (400.13 MHz, [D_1]chloroform, 25 °C): $\delta = -1.27$ (bs, 2H; cage CH), 1.59 ppm (s, 30H; C_5Me_5); $^{11}B\{^1H\}$ NMR (128.38 MHz, [D_1]chloroform, 25 °C): $\delta = -5.62$ (2B), 17.78 (4B), 36.37 (2B), 97.03 ppm (1B); elemental analysis (%) calcd: C 43.68, H 6.83, B 16.08; found: C 43.65, H 6.78, B 15.98.

Analogously, direct reaction of [{(η-C_5Me_5)RuCl}$_4$] (82 mg, 0.075 mmol) and Tl[Tl($C_2B_9H_{11}$)] (81 mg, 0.15 mmol) in THF or Me_2CO gave **2b** (64 mg, 70 %).

Complex **2b** was also prepared in 55 % yield starting from [(η-C_5Me_5)-Ru(MeCN)$_3$]CF_3SO_3, similar to preparation of **2a**.

Received: July 9, 2002 [Z19691]

---

[1] R. N. Grimes in *Comprehensive Organometallic Chemistry 1, Vol. 1* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, New York, **1982**, p. 459.

[2] a) V. R. Miller, L. G. Sneddon, D. C. Beer, R. N. Grimes, *J. Am. Chem. Soc.* **1974**, *96*, 3090; b) W. M. Maxwell, E. Sinn, R. N. Grimes, *J. Am. Chem. Soc.* **1976**, *98*, 3490; c) M. Green, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc. Daton Trans.* **1979**, 1679, and references therein; d) G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc. Chem. Commun.* **1983**, 137; e) M. P. Garcia, M. Green, F. G. A. Stone, R. G. Somerville, A. J. Welch, C. E. Briant, D. N. Cox, D. M. P. Mingos, *J. Chem. Soc. Dalton Trans.* **1985**, 2343.

[3] An indirect insertion, based on two-electron reduction of *closo*-carborane or metallacarborane with subsequent treatment of *nido*-anion formed with a metal electrophile, is well known. For example: a) D. F. Dustin, G. B. Dunks, M. F. Hawthorne, *J. Am. Chem. Soc.* **1973**, *95*, 1109; b) W. J. Evans, M. F. Hawthorne, *Inorg. Chem.* **1974**, *13*, 869.

[4] a) A. R. Kudinov, M. I. Rybinskaya, Yu. T. Struchkov, A. I. Yanovskii, P. V. Petrovskii, *J. Organomet. Chem.* **1987**, *336*, 187; b) P. O. Lumme, U. Turpeinen, A. R. Kudinov, M. I. Rybinskaya, *Acta Crystallogr. Sect. C* **1990**, *46*, 1410.

[5] R. S. Coldicott, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.* **1996**, 3819.

[6] C. G. Salentine, M. F. Hawthorne, *Inorg. Chem.* **1978**, *17*, 1498.

[7] Crystallographic data for PPN-**1**: at 295 K crystals of $C_{48}H_{56}B_9NP_2Ru$ are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 16.800(3)$, $b = 16.044(3)$, $c = 18.490(4)$ Å, $\beta = 109.152(5)°$, $V = 4707.7(15)$ Å^3, $\mu(Mo_{K\alpha}) = 4.36$ cm^{-1}. Intensities of 26827 reflections were measured with a Smart 1000 CCD diffractometer at 295 K ($\lambda(Mo_{K\alpha}) = 0.71073$ Å, $2\theta < 50°$), and 8271 independent reflections ($R_{int} = 0.0603$) were used in further refinement. One of the two carbon atoms in the cage was assumed to be disordered and occupied positions adjacent to either side of C(1). In the subsequent refinements each of the disordered atoms was assigned the scattering power of an atom that was half boron and half carbon. The refinement converged to $wR_2 = 0.0973$ and $GOF = 0.992$ for all independent reflections ($R1 = 0.0487$ was calculated against F for 4518 observed reflections with $I > 2\sigma(I)$). Crystallographic data for **2b**: at 140 K crystals of $C_{22}H_{41}B_9Ru_2$ are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.3431(13)$, $b = 15.782(3)$, $c = 20.446(3)$ Å, $\beta = 101.483(3)°$, $V = 2638.4(7)$ Å^3, $\mu(Mo_{K\alpha}) = 11.55$ cm^{-1}. Intensities of 30997 reflections were measured with a Smart 1000 CCD diffractometer at 140 K ($\lambda(Mo_{K\alpha}) = 0.71073$ Å, $2\theta < 60°$), and 7647 independent reflections ($R_{int} = 0.0325$) were used in further refinement. The refinement converged to $wR_2 = 0.0981$ and $GOF = 1.040$ for all independent reflections ($R1 = 0.0414$ was calculated against F for 6443 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL 5.1. CCDC-188268 (PPN-**1**) and CCDC-188269 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[8] D. C. Liles, A. Shaver, E. Singleton, M. B. Wiege, *J. Organomet. Chem.* **1985**, *288*, C33.

[9] a) R. T. Baker, *Inorg. Chem.* **1986**, *25*, 109; b) R. L. Johnston, D. M. P. Mingos, *Inorg. Chem.* **1986**, *25*, 3321; c) M. L. McKee, Z.-X. Wang, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2000**, *122*, 4781, and references therein.

[10] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[11] P. W. Fowler, *Polyhedron* **1985**, *4*, 2051.

Conformation-Dependent Ionization Energies of L-Phenylalanine**

Kang Taek Lee, Jiha Sung, Kwang Jun Lee,
Young Dong Park, and Seong Keun Kim*

In recent years there has been an outburst of research interest in small biological molecules in the gas phase.[1] By placing these molecules on the "transparent cover glass" of an isolated environment, one can unravel intrinsic properties usually hidden in the complex medium of a real biological system. The need for such gas-phase studies arises from the anticipation that many biological phenomena can be traced to the fundamental properties of the molecular constituents. Both laser spectroscopy and theoretical methods have made great contributions to elucidating the structures and dynamics of nonrigid biomolecules and their solvated complexes in the gas phase.[2]

Amino acids are known to exist in various conformations resulting from the flexibility of their structures, which comprise a backbone and a side chain or residue. The conformational variety of amino acids plays a crucial role in determining the three-dimensional structure of proteins and controlling their dynamics.[3] The energy barrier that separates different conformers is typically rather small so that thermal energy at room temperature enables the molecule to freely change from one conformation to another. Therefore, it is not generally feasible to isolate a specific conformer experimentally at room temperature. By employing a supersonic expansion, however, one can cool down the molecule to a temperature low enough to isolate it in various frozen forms, in other words, as individual conformers. Numerous exper-

---

[*] Prof. Dr. S. K. Kim, K. T. Lee, J. Sung, K. J. Lee
School of Chemistry, Seoul National University
Seoul 151-747 (Korea)
Fax: (+82) 2-889-5719
E-mail: seongkim@plaza.snu.ac.kr

Prof. Dr. Y. D. Park
Department of Chemistry, Ajou University
Suwon, Kyunggi-do 442-749 (Korea)

[**] This work was supported by the National Creative Research Initiatives Program (99-C-CT-01-C-50) of the Ministry of Science and Technology of Korea.

imental studies have dealt with amino acids and their conformers in the gas phase.[4–15]

Another interesting subject involves amino acids that carry a whole ionic charge since electrostatic interactions are ubiquitous in many proteins and affect their structures and functions. Many gas-phase studies on ionic amino acids, peptides, and proteins have focused on protonated cations or metal ion complexes, but to our knowledge, an unadulterated ionic amino acid has not yet been studied, presumably because of the difficulties in producing an intact ion in the gas phase.

Here we report a study on the photoionization of the aromatic amino acid phenylalanine (Phe) generated by supersonic expansion. We measured the ionization energies (IEs) of all low-energy conformers by resonant two-photon ionization (R2PI). This revealed strikingly different IE values that range from 8.80 to 9.15 eV. We found that a very strong correlation exists between the IE of a given conformer and how its backbone interacts with the side chain.

Figure 1 depicts the six lowest energy conformational structures of Phe as determined by Simons and co-workers; they are shown here for expedient reference.[13] They can be divided into two subgroups according to the intramolecular hydrogen-bonding scheme. In the first subgroup (subgroup I) consisting of the conformers X, B, and E, the carboxy hydrogen atom forms a hydrogen bond with the nonbonding electrons of the amino group. Additionally, an amino hydrogen atom interacts with the phenyl ring in what appears to be a π–hydrogen bond, thereby forming a complete sequence of hydrogen bonds, COOH→NH_2→π. The strength of the latter hydrogen bond, NH_2→π should be enhanced by the former hydrogen bond, COOH→NH_2, which endows the amino hydrogen atom with a stronger positive charge.[13] Thus these two hydrogen bonds act cooperatively in determining the structure of the conformers in the first subgroup. In the other subgroup (subgroup II), which includes the conformers A, C, and D, the direction of the hydrogen bonding is reversed between the amino and the carboxy group, that is, NH_2→COOH, whether it involves only a single or both hydrogen atoms of the amino group. In these conformers the carboxy hydrogen atom remains free and does not interact with the phenyl ring. This means that there is little interaction between the residue and the backbone through either the carboxy group or the amino group.

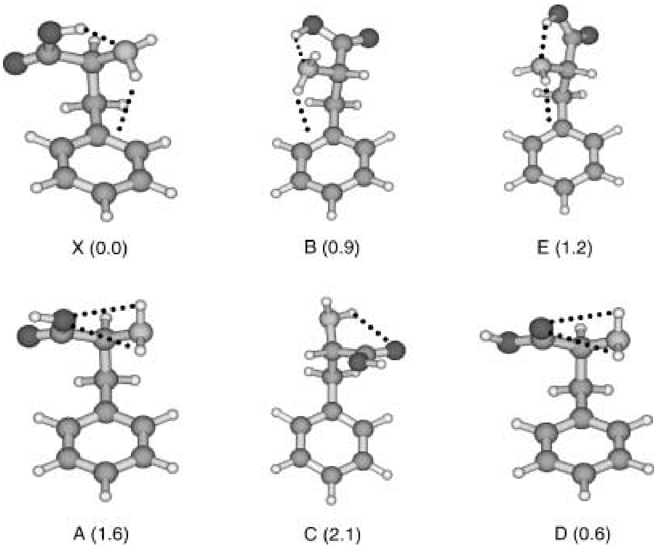


Figure 1. Geometries of the six most stable Phe conformers optimized at the B3LYP/6-31 + G(d) level. The labels are adopted from reference [13]. In parentheses are shown the relative energies (in kcal mol^{-1}) calculated at the MP2/6-311G(d,p) level with the zero-point energy corrections (B3LYP/6-31 + G(d)).

In a recent paper[15] we pointed out that this grouping of Phe conformers may be incorrect with regard to conformer E. We proposed that conformer E should be included in subgroup II rather than subgroup I, with hydrogen bonding from the amino to the carboxy group, based on our observation that conformer E binds water just as efficiently as members of subgroup II and much more efficiently than those of subgroup I. Theoretical calculations predict that all conformers of subgroup II interact more strongly with water than those of subgroup I because water tends to make a hydrogen bond with the free carboxy hydrogen atom. As will be discussed later, this proposition is further corroborated by new findings in the present study. Our regrouping of the conformers would classify A, C, D, and E as subgroup II and X and B as subgroup I.

Figure 2a shows a one-color R2PI excitation spectrum of Phe in the S_1 origin region. The six peaks are the band origins of the corresponding six lowest energy conformers shown in Figure 1, with the structure of conformer E undetermined as described above. The adiabatic IE of Phe is known to be 8.5 eV,[16] but its vertical IE is not yet known. Since the one-color two-photon energy (~ 9.4 eV) could be well above the vertical IE, we employed two-color R2PI to reduce the excess energy above the ionization threshold. Figure 2b displays a two-color R2PI excitation spectrum obtained at conditions similar to those given in Figure 2a but with the ionization laser fixed at 285.5 nm. Strikingly, the bands B and X are totally missing in this spectrum, while all other bands are observed with nearly the same intensity ratio as in the one-color spectrum. We note that the band E behaves more like those of subgroup II than of subgroup I. The peak at 37 646 cm^{-1} in Figure 2a, which is known to be a low-frequency vibration of X,[13] also disappears in Figure 2b.

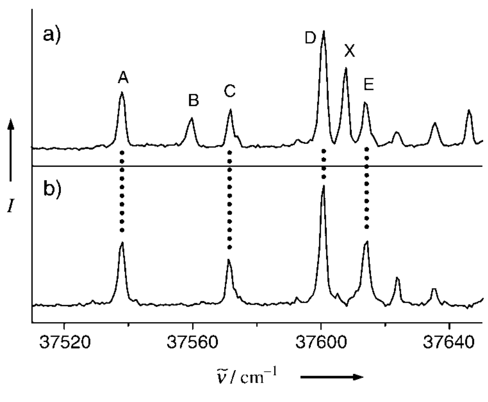


Figure 2. Mass-resolved R2PI excitation spectra of jet-cooled Phe obtained by a) one-color and b) two-color ionization. The wavelength of the ionization laser was fixed at 285.5 nm in (b).

The absence of the bands associated with the two conformers B and X, in contrast to the presence of the bands for A, C, D, and E in Figure 2b, must mean that the two-photon energy here (~9.0 eV) is smaller than the IEs of the conformers B and X but still larger than those of the other four conformers.

To further confirm this observation we obtained the photoionization efficiency (PIE) curves for all six conformers (Figure 3). For each curve the wavelength of the excitation laser was fixed at the S_1 band origin of the corresponding conformer, thus the selection of the species being ionized is achieved in the first excitation step. Here, too, band E behaves like a member of subgroup II along with the bands A, C, and D. All the PIE curves are seen to have a very gradual increase in the ion signal and a poorly defined ionization threshold. This feature can be explained by a poor Franck–Condon factor for ionization, as in similar cases of 2-phenylethylamine (PEA),[17] benzyl and salicyl alcohol,[18] and *p*-methoxyphenethylamine.[19] It has been recognized for such molecules that the minima of the neutral and the cationic potential energy surfaces (PES) are much displaced from each other. A cation is thus produced at a repulsive part of the PES, where the density of states is very high at a considerable internal energy which leads to a broad and structureless band profile in the photoion or photoelectron spectra.

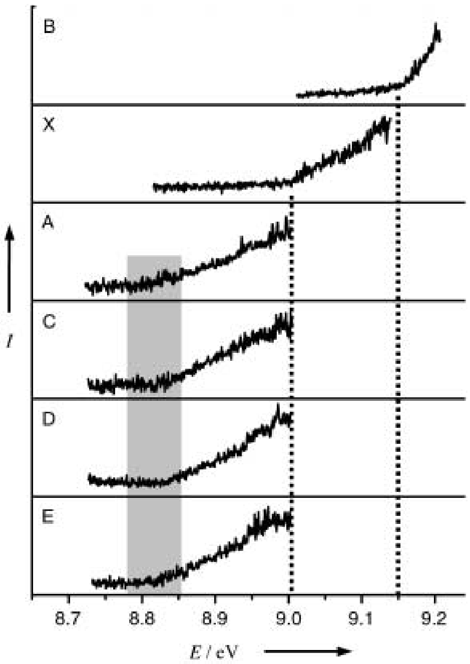


Figure 3. PIE curves of the Phe conformers. Each curve was obtained by scanning the wavelength of the ionization laser across the IE while fixing the wavelength of the excitation laser at the S_1 band origin of the labeled conformer.

Conformers B and X of subgroup I have IEs of 9.15 and 9.00 eV, respectively, much larger than the nearly identical IEs of ~8.8 eV for all the conformers of subgroup II. That is indeed the reason for the absence of the bands B and X in the two-color R2PI excitation spectrum in Figure 2b. If we classified the conformers into two different subgroups only on the basis of the magnitude of IE, we would have two subgroups, (A, C, D, E) vs. (B, X). It is very interesting that this classification by IE gives the same result as our earlier classification of the Phe conformers on the basis of the propensity of Phe toward hydration. Hydration was found to take place only with A, C, D, and E but not with B and X,[15] which was suggested to result from the different hydrogen-bonding schemes resulting from the different geometries between the two subgroups. Likewise, the higher IEs of B and X should also reflect the structural difference between the two subgroups.

As already mentioned with regard to Figure 1, there is an additional hydrogen bond for B and X between the amino group and the phenyl ring in addition to, and enhanced by, the hydrogen bond between the carboxy and amino groups. When B and X are ionized by two-photon ionization via the $\pi\pi^*$ resonance state (S_1), the phenyl ring would attain a positive charge, at least partially, which will turn the attractive interaction between the amino hydrogen atom and the phenyl ring into a repulsive one. In contrast conformers A, C, D, and E would be little influenced by the positive charge on the phenyl ring since the interaction between the backbone and the phenyl ring is much weaker for these conformers in the first place in their neutral state. Therefore, the nascent cations of B and X are expected to be higher in energy than the other conformers because of their repulsive backbone–π interaction, which also leads to the higher IEs.

The conformer-dependent IEs have been observed recently for molecules such as 1-iodopropane,[20] 9-ethylfluorene,[21] *p*-methoxyphenethylamine,[19] and formanilide.[22] However, the difference between the IEs of different conformers is generally small for these molecules, mostly below ~300 cm^{-1}. By comparison, the difference of up to 0.35 eV (~2800 cm^{-1} or 8 kcal mol^{-1}) in the IEs of the two subgroups of Phe conformers is remarkably large—an order of magnitude greater than all the known cases.

In summary, we employed the technique of supersonic jet cooling for Phe to freeze out its various conformational structures and used R2PI to measure the IE for specific conformations. We found that the IE is very much conformation-dependent, ranging from 8.80 to 9.15 eV. The magnitude of the differences in the IEs exceeds the largest value reported to date for a conformation-dependent IE of any molecule by an order of magnitude. Two distinct subgroups were proposed for the six lowest energy conformers of Phe on the basis of the magnitude of IE, which turned out to give the same classification as that derived from the conformation-dependent propensity toward hydration. The culprit for the large variances in the IEs as well as the propensities for hydration was the drastically different nature of hydrogen bonding between the two subgroups of conformers. It reflects the large conformational change upon ionization, the effect of which is maximized in the present case of Phe because of the characteristically strong intramolecular hydrogen bonds typically found in amino acids.

Experimental Section

The experimental setup used in this study has been described in detail.[15] Phe powder was vaporized by heating the oven to 180 °C and expanded through a pulsed nozzle with a 0.8-mm hole by using neon carrier gas at

1 atm. The Phe sample was purchased from Aldrich Chemical Company and used without further purification.

Received: May 15, 2002 [Z19307]

---

[1] C. Desfrançois, S. Carles, J. P. Schermann, *Chem. Rev.* **2000**, *100*, 3943.
[2] E. G. Robertson, J. P. Simons, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1.
[3] J. M. Berg, J. L. Tymoczko, L. Stryer, *Biochemistry*, 5th ed., Freeman, New York, **2002**.
[4] R. D. Suenram, F. J. Lovas, *J. Am. Chem. Soc.* **1980**, *102*, 7180.
[5] P. D. Godfrey, S. Firth, L. D. Hatherley, R. D. Brown, A. P. Pierlot, *J. Am. Chem. Soc.* **1993**, *115*, 9687.
[6] T. R. Rizzo, Y. D. Park, L. A. Peteanu, D. H. Levy, *J. Chem. Phys.* **1986**, *84*, 2534.
[7] L. Li, D. M. Lubman, *Appl. Spectrosc.* **1988**, *42*, 418.
[8] C. K. Teh, J. Sipior, M. Sulkes, *J. Phys. Chem.* **1989**, *93*, 5393.
[9] S. J. Martinez III, J. C. Alfano, D. H. Levy, *J. Mol. Spectrosc.* **1992**, *156*, 421.
[10] A. Lindinger, J. P. Toennies, A. F. Vilesov, *J. Chem. Phys.* **1999**, *110*, 1429.
[11] R. Cohen, B. Brauer, E. Nir, L. Grace, M. S. de Vries, *J. Phys. Chem. A* **2000**, *104*, 6351.
[12] F. Piuzzi, I. Dimicoli, M. Mons, B. Tardivel, Q. Zhao, *Chem. Phys. Lett.* **2000**, *320*, 282.
[13] L. C. Snoek, E. G. Robertson, R. T. Kroemer, J. P. Simons, *Chem. Phys. Lett.* **2000**, *321*, 49.
[14] L. C. Snoek, R. T. Kroemer, M. R. Hockridge, J. P. Simons, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1819.
[15] K. T. Lee, J. Sung, K. J. Lee, S. K. Kim, Y. D. Park, *J. Chem. Phys.* **2002**, *116*, 8251.
[16] S. Campbell, J. L. Beauchamp, M. Rempe, D. L. Lichtenberger, *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 83.
[17] R. Weinkauf, F. Lehrer, E. W. Schlag, A. Metsala, *Faraday Discuss.* **2000**, *115*, 363.
[18] C. E. H. Dessent, W. D. Geppert, S. Ullrich, K. Müller-Dethlefs, *Chem. Phys. Lett.* **2000**, *319*, 375.
[19] I. Unamuno, J. A. Fernández, A. Longarte, F. Castaño, *J. Phys. Chem. A* **2000**, *104*, 4364.
[20] S. T. Park, S. K. Kim, M. S. Kim, *J. Chem. Phys.* **2001**, *114*, 5568.
[21] J. D. Pitts, J. L. Knee, S. Wategaonkar, *J. Chem. Phys.* **1999**, *110*, 3378.
[22] S. Ullrich, G. Tarczay, X. Tong, C. E. H. Dessent, K. Müller-Dethlefs, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5450.

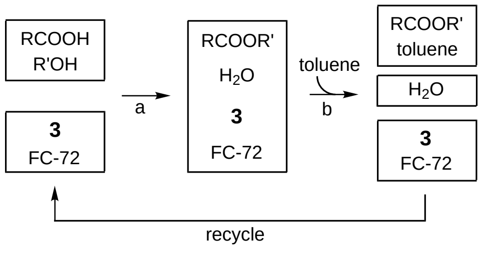
Fluorous Biphasic Esterification Directed towards Ultimate Atom Efficiency**

Jiannan Xiang, Akihiro Orita, and Junzo Otera*

Esterification technology is currently undergoing intensive innovation to meet the rapidly increasing demands for sustainable chemistry.[1] Since the direct reaction between a carboxylic acid and an alcohol is innately an equilibrium process, high atom efficiency[2] is not easy to achieve: either of the reactants must be used in excess and/or the water formed must be removed constantly during the reaction to bias the equilibrium to the product side. In particular, the direct condensation between carboxylic acids and alcohols with a strict 1:1 stoichiometry by use of a simple catalyst system is very difficult to complete, although activation of the carboxylic acid component with a stoichiometric amount of promoter such as DCC[3] or DEAD[4] is another possible but uneconomical choice. In this context, graphite bisulfate was reported to catalyze esterification between equimolar reactants.[5] Later, microwave irradiation coupled with *p*-toluenesulfonic acid catalyst was reported.[6] Recently, a few more related catalysts have appeared. Although the Soxhlet technique must be invoked, $NaHSO_4 \cdot H_2O$[7] and $HfCl_2 \cdot 2\,THF$[8] were found to work well as a catalyst. On the other hand, $Ph_2NH_2^+OTf^-$ served for the present purpose without recourse to any dehydration reagents or apparatus.[9] The yields of all of these reactions were high (mostly > 85 %) but, unfortunately, not perfectly quantitative, except for two cases in the $HfCl_2 \cdot 2\,THF$ protocol (> 99 %). This is somewhat problematic, not only in view of atom efficiency but also of practical operation. The 1:1 stoichiometry is truly effective only if 100 % conversion is reached. In this case, the product ester constitutes a sole organic component in the reaction mixture, but otherwise separation of the remaining carboxylic acid and alcohol from the product mixture is unavoidable. As a consequence, an ideal goal of esterification would be 100 % yield by use of equimolar reactants without recourse to any dehydration technique.

Recently, we disclosed that the fluorous biphasic transesterification by use of fluoroalkyldistannoxane catalysts gave rise to virtually 100 % yields with ester and alcohol reactants in a 1:1 ratio.[10] It was suggested in this protocol that liberation of a lighter alcohol from the equilibrium system as a result of its lower solubility in fluorocarbon solvents facilitated the conversion in favor of the esters with a higher alcohol component. Since water is much less fluorophilic than alcohols, we postulated that the condensation between carboxylic acids and alcohols should proceed more efficiently. We report herein the first fluorous biphasic esterification that achieves the above-mentioned goal. Furthermore, facile separation of the catalyst is another notable advantage that results from the fluorous biphasic technology.

As shown in Scheme 1, an equimolar mixture of RCOOH (**1**) and R′OH (**2**) together with $[\{Cl(C_6F_{13}C_2H_4)_2SnOSn(C_2H_4C_6F_{13})_2Cl\}_2]$ (**3**)[11] (5 mol %) in FC-72 (perfluorohexanes) was heated at 150 °C. After being cooled to room temperature, toluene was added to the



Scheme 1. Esterification in a biphasic system. Reagents and conditions: a) acid (2.0 mmol), alcohol (2.0 mmol), **3** (0.1 mmol), FC-72 (5 mL), 150 °C, 16 h; b) extraction with toluene (5 mL and 2 × 2 mL).

---

[*] Prof. Dr. J. Otera, J. Xiang, Dr. A. Orita
Department of Applied Chemistry, Okayama University of Science
Ridai-cho, Okayama 700-0005 (Japan)
Fax: (+81) 86-256-4292
E-mail: otera@high.ous.ac.jp

[**] This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.