quoted are accurate to ±10-15%.

(11) After reaction times of more than 6 h, 1 is gradually decomposed with an accompanying loss of activity for Ph_3P oxidation. After 48 h, when 1 is completely decomposed, oxidation of Ph_3P in the presence of O_2 is not observed.

(12) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Am. Chem. Soc.*, **93**, 1374 (1971).

(13) $Co(saloph)\cdot PPh_3\cdot NO_2$ is prepared in manner similar to the preparation of 1: ν_{NO_2} 1305, 1225, 810 cm^{-1}.

(14) R. Barral, C. Bocard, I. S. de Roch, and L. Sajus, *Tetrahedron Lett.*, **17**, 1693 (1972); P. C. H. Mitchell and R. D. Searle, *J. Chem. Soc., Dalton Trans.*, 2552 (1975); G. J. J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).

(15) This sytem may be compared with the recently reported oxidation of PPh_3 to $OPPh_3$ by a Ru-NO_2 complex.[16] The oxidant $[Ru^{III}(bpy)_2NO_2Cl]^+$ is generated electrochemically from $[Ru^{II}(bpy)_2(NO)Cl]^{2+}$ in the presence of water and a base. In this system, oxidizing equivalents are provided electrochemically instead of by O_2, and 1 mol of hydroxide is needed for every mole of $OPPh_3$ produced.

(16) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.* **99**, 4821 (1977).

(17) NOTE ADDED IN PROOF. Recently H. Mimoun and co-workers (*J. Am. Chem. Soc.*, **100**, 5437 (1978)) described the specific oxidation of terminal olefins to 2-alkanones employing Rh-based catalysts in which terminal olefins are the only oxidizable ligands.

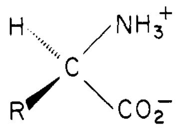
Benjamin S. Tovrog,* Steven E. Diamond, Frank Mares
Allied Chemical Corporation, Chemical Research Center
Morristown, New Jersey 07960

Received August 13, 1978

Experimental Determination of the Acidity and Basicity of Glycine in the Gas Phase

Sir:

For many years it has been known that the most stable structure of α-amino acids in aqueous solution and in the crystalline state is best written as a dipolar ion, or zwitterion.



Typically these compounds are appreciably soluble only in water, and as solids they do not melt until they decompose at almost 300 °C.[1] These physical properties are consistent with the "salt-like" dipolar ion structure. There are two ionizable groups in aqueous solution having pK_a values of 2 and 9. Taking glycine as an example, the first pK_a at 2.3 is what one expects for ionization of a carbonyl group (reaction 1). This

$$H_3\overset{+}{N}CH_2COOH = H^+ + H_3\overset{+}{N}CH_2COO^-, \quad \Delta G^\circ = 3.1 \text{ kcal/mol} \quad (1)$$

pK_a value is consistent with that of acetic acid (pK_a = 4.8) and the presence of a strong electron-withdrawing effect of the positive ammonium group which stabilizes the glycine dipolar ion.[1] The second acid dissociation for glycine has a pK_a of 9.6 and corresponds to reaction 2. This is similar to ethaneammonium ion having a pK_a of 10.7. Thus, in aqueous solution the basicity of glycine (reaction 1) is similar to that of acetate ion, and the acidity of glycine (reaction 2) is similar to that of an alkylammonium ion.

$$H_3\overset{+}{N}CH_2COO^- = H^+ + H_2NCH_2COO^-, \quad \Delta G^\circ = 13 \text{ kcal/mol} \quad (2)$$

Very little is known about the properties of α-amino acids in the gas phase owing to their extremely low volatility and tendency to decompose at elevated temperatures. Electron impact mass spectrometry on glycine produces a base peak at *m/e* 30, $H_2NCH_2^+$, corresponding to loss of COOH from the neutral molecule.[2] Chemical ionization mass spectrometry using methane,[3] isobutane,[4] and hydrogen[5] as reagent gases has been performed to elaborate the fragmentation mechanisms. However, there are no data in the literature which allow the acidity and basicity of the α-amino acids in the gas phase to be compared with the energetics of their ionization in aqueous solution.

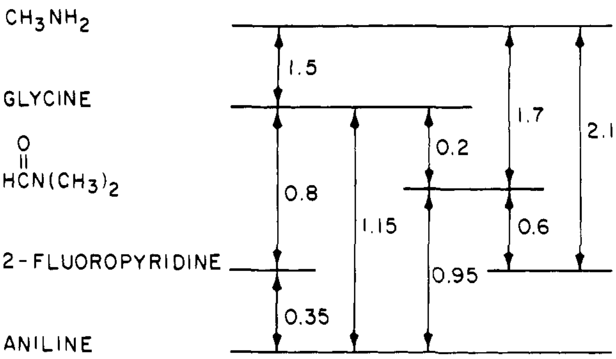


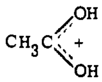
Figure 1. The basicity of the α-amino acid glycine in the gas phase relative to several reference bases previously studied by the equilibrium pulsed ICR technique. Each number listed is the result of a separate determination of $\Delta G_{382}°$ (kilocalories/mole) for proton transfer reactions such as $AH^+ + B = BH^+ + A$. The strongest base in this series is CH_3NH_2.

In this communication we report for the first time measurements of the gas-phase acidity and basicity of glycine. The experiments were performed with a specially constructed pulsed ion cyclotron resonance (ICR) spectrometer having a heated analyzer system. The procedures used to study the gaseous positive and negative ions of glycine were identical with those previously described in detail,[6] with the exception that the analyzer system was heated and the glycine sample was admitted to the spectrometer via a direct insertion probe. Each glycine sample was thoroughly dried to remove water. Electron impact ionization at 20 eV confirmed the presence of the base peak for glycine at *m/e* 30 and the absence of water. Under typical operating conditions of 109 °C, the pressure of glycine in the ICR analyzer cell was 1 × 10^{-6} Torr as measured by a Bayard-Alpert ionization gage.

Data for the equilibrium relative basicity of glycine in the gas phase are shown in Figure 1. Multiple determinations were made using four reference bases to ensure the reliability of the measurements. Glycine is found to be slightly less basic than methylamine. Based upon a value of 207.0 kcal/mol for the proton affinity of ammonia ($\Delta H_{298}°$ for $NH_4^+ = NH_3 + H^+$), the energetics for the gas-phase protonation reactions are as shown in reactions 3-5.[7] It is obvious from comparison of reaction 1 and reaction 3 that the basicity of glycine in the gas phase is enormously greater than in aqueous solution. This is primarily due to the high solvation energy of the proton. Of greater interest, however, is the finding that the gas-phase basicity of glycine is more similar to that of methylamine than acetic acid. We conclude from these data that in the gas phase glycine protonates on the α-amino group to produce the ionic structure shown in reaction 3.

$$H_3\overset{+}{N}CH_2COOH = H^+ + \text{glycine}, \quad \Delta G^\circ_{382} = 205.8 \text{ kcal/mol} \quad (3)$$

$$CH_3NH_3^+ = H^+ + CH_3NH_2, \quad \Delta G^\circ_{382} = 207.3 \text{ kcal/mol} \quad (4)$$



$$CH_3C(OH)_2^+ = H^+ + CH_3COOH, \quad \Delta G^\circ_{382} = 184.3 \text{ kcal/mol} \quad (5)$$

It has also been possible to measure the gas-phase acidity of glycine, and these data are shown in Figure 2. Glycine is a stronger acid than both acetic and formic acid in the gas phase. Based upon a value of 329.6 kcal/mol for the acidity of benzoic acid at 385 K, the energetics of the gas-phase deprotonation reactions are as shown in reactions 6-8.[8] It is apparent from reaction 6 that heterolytic bond dissociation, $AH = H^+ + A^-$, is a far more endothermic process in the gas phase than in aqueous solution (reaction 2). These data also show that gly-

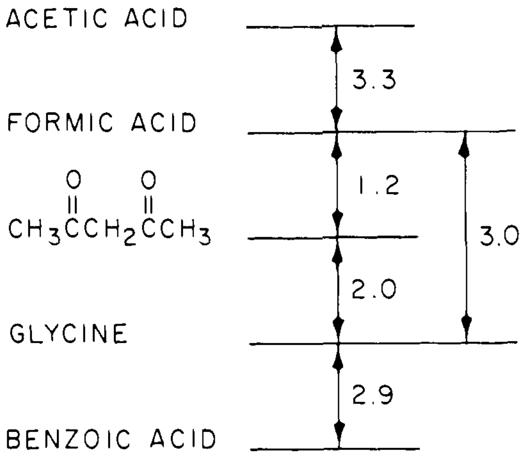


Figure 2. The acidity of glycine in the gas phase realtive to several reference acids. Each number listed is $\Delta G_{385}°$ (kilocalories/mole) for proton transfer reactions such as $A^- + BH = B^- + AH$. The strongest acid in this series is benzoic acid.

$$\text{glycine} = H^+ + H_2NCH_2COO^-, \quad \Delta G^\circ_{385} = 332.5 \text{ kcal/mol} \tag{6}$$

$$CH_3COOH = H^+ + CH_3COO^-, \quad \Delta G^\circ_{385} = 339.0 \text{ kcal/mol} \tag{7}$$

$$CH_3NH_2 = H^+ + CH_3NH^-, \quad \Delta G^\circ_{385} = 393.5 \text{ kcal/mol} \tag{8}$$

cine in the gas phase has a deprotonation energy more similar to acetic acid than methylamine. Thus, we conclude that the $(M - H)^-$ ion of glycine is due to loss of a proton from the carbonyl group to give the ionic structure shown in reaction 6.

The site of protonation and the site of deprotonation of glycine in the gas phase are established by the comparisons made above. Furthermore, glycine in the gas phase behaves in its acid/base chemistry like a nonionic α-aminocarboxylic acid rather than a zwitterion. Matrix isolation studies[9] and recent theoretical calculations[10] also indicate that the nonionic form is more stable than the dipolar form. We are currently investigating this problem in more detail by studying the effects of substituents on the gas-phase acidity and basicity of α-amino acids.

Acknowledgments. This work was supported by grants from the National Science Foundation (CHE77-10024) and the National Institutes of Health (GM23416-02).

References and Notes

(1) See, for example, J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids", Vol. 1, Wiley, New York, N.Y., 1961, Chapter 4, pp 497–500.
(2) (a) G. Junk and H. Svec, *J. Am. Chem. Soc.*, **85**, 839 (1963); (b) K. Biemann and J. A. McCloskey, *ibid.*, **84**, 3192 (1962).
(3) (a) G. W. A. Milne, T. Axenrod, and H. M. Fales, *J. Am. Chem. Soc.*, **92**, 5170 (1970); (b) P. A. Lechercq and D. M. Desiderio, *Org. Mass Spectrom.*, **7**, 515 (1973).
(4) M. Meot-Ner and F. H. Field, *J. Am. Chem. Soc.*, **95**, 7207 (1973).
(5) C. W. Tsang and A. G. Harrison, *J. Am. Chem. Soc.*, **98**, 1301 (1976).
(6) (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1978); (b) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
(7) In recent months the preferred value for the gas-phase proton affinity of ammonia ($\Delta H_{298}°$ for $NH_4^+ = NH_3 + H^+$) has begun to inflate once again after an extended period of stability. The relative proton affinity scales reported by ref 6b and R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976), have been shifted up in absolute value owing to revised values for certain of the reference compounds. In particular, revised values for $\Delta H_f°$ (t-$C_4H_9\cdot$) and the ionization potential of t-$C_4H_9\cdot$ have changed the proton affinity of isobutene from 193.0 to 197.4 kcal/mol, and this shifts the PA (NH_3) from the previously accepted value of 202.3 to 206.7 kcal/mol. Since this situation still seems to be unresolved, we have simply selected 207.0 kcal/mol as our reference value for ammonia. Conversion from $\Delta H_{298}°$ to $\Delta G_{382}°$ for the process $NH_4^+ = NH_3 + H^+$ can be accomplished by estimating the entropy of this reaction to be equal to $S°(H^+) + R \ln (3/12)$, where 3/12 is the ratio of the rotational symmetry numbers for NH_3 and NH_4^+, respectively. Thus, at 382 K, $\Delta G_{382}° = 207.0 - 0.382\,(26.043 + R \ln 3/12) = 198.1$ kcal/mol for the gas-phase basicity of ammonia. Of course, the relative values reported in Figure 1 are not affected by changes in the absolute values of the reference compounds.
(8) The value 329.6 kcal/mol for the absolute acidity of benzoic acid is due to equilibrium measurements by Cumming and Kebarle, *Can. J. Chem.*, **56**, 1 (1978), and the acidity of CH_3NH_2 was measured by G. I. Mackay, R. S. Hemsworth, and D. K. Bohme, *Can. J. Chem.*, **54**, 1624 (1976).
(9) Y. Grenie, J.-C. Lassegues, and C. Garrigou-Lagrange, *J. Chem. Phys.*, **53**, 2980 (1970).
(10) Y.-C. Tse, M. D. Newton, S. Vishveshware, and J. A. Pople, *J. Am. Chem. Soc.*, **100**, 4329 (1978).

Michael J. Locke, Richard L. Hunter
Robert T. McIver, Jr.*
Department of Chemistry, University of California
Irvine, California 92717

Received October 15, 1978

Photoactivation of Cluster Catalysis: a Comparison of 1-Pentene Isomerization by Tetracarbonyl(triphenylphosphine)ruthenium and 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2,3-tris(triphenylphosphine)-*triangulo*-triruthenium

Sir:

In this communication we register two potential advantages of cluster precursors to photochemically generated catalysts. We present preliminary results demonstrating that (1) lower energy irradiation can be used to activate catalysis by irradiation of a cluster compared with an appropriate mononuclear analogue and (2) the active species generated from the cluster can operate on the substrate to give a substantially different ratio of products. The latter result bears on the question of whether cluster species can do unique chemistry relative to their mononuclear fragments. We report a comparison of the photocatalyzed 1-pentene isomerization by $Ru_3(CO)_9(PPh_3)_3$ and $Ru(CO)_4(PPh_3)$.[1]

Before detailing the results concerning the 1-pentene isomerization, we will delineate some of the essential photochemical and spectral properties of the two catalyst precursors. Both complexes are thermally inert at 298 K, but each is photosensitive. The absorption spectra of the two complexes are included in Figure 1; $Ru(CO)_4(PPh_3)$ is a pale yellow substance with only tail absorption at wavelengths longer than 300 nm, while $Ru_3(CO)_9(PPh_3)_3$ exhibits an intense visible absorption maximum at 506 nm (ε ~14 000). The ultraviolet absorption of the C_{3v} $Ru(CO)_4(PPh_3)$ is logically a ligand field transition which terminates in the d_{z^2} orbital which is strongly σ antibonding.[2] Near-UV, 355 nm, irradiation in the presence of added 0.1 M PPh_3 in benzene yields $Ru(CO)_3(PPh_3)_2$ (ν_{CO} 1895 cm^{-1}),[3] and irradiation in the presence of 0.1 M $P(OMe)_3$ in benzene apparently yields $Ru(CO)_3(PPh_3)[P(OMe)_3]$ (ν_{CO} 1905 cm^{-1}) and *not* $Ru(CO)_4[P(OMe)_3]$. These results allow the conclusion that loss of CO is the principal result of near-UV irradiation of $Ru(CO)_4(PPh_3)$ (eq 1).

$$Ru(CO)_4(PPh_3) \xrightarrow[355\ \text{nm}]{h\nu} Ru(CO)_3(PPh_3) + CO \tag{1}$$
$$\Phi = 0.32 \pm 0.02$$

When CO is purged from the solution, 1-pentene can scavenge $Ru(CO)_3(PPh_3)$ to yield a very substitution labile 1-pentene complex, but, in hermetically sealed samples of benzene solutions of 1.76 M 1-pentene, $Ru(CO)_4PPh_3$ undergoes little net reaction even at long irradiation times. Note that the coordinatively unsaturated species generated has the same empirical formula as $Ru_3(CO)_9(PPh_3)_3$. This fact is an important feature of the system under study, since we find that visible irradiation of $Ru_3(CO)_9(PPh_3)_3$ in the presence of L yields $Ru(CO)_3PPh_3L$, (eq 2). Based on this photochemistry

$$Ru_3(CO)_9(PPh_3)_3 \xrightarrow[L=CO,\ PPh_3]{h\nu,\ 514.5\ \text{nm}} 3Ru(CO)_3PPh_3L \tag{2}$$
$$\Phi \approx 10^{-2}$$