spectroscopy. Photolysis of **4**-d_2 isolated in an argon matrix at 10 °K results in product bands at 2109, 1599, 1571, 1195, 913, 900, and 794 cm^{-1} plus the CO band at 2141 cm^{-1}. The bands at 1599 and 1571 cm^{-1} are in the N=N stretch region. Irradiation of **4**-^{15}N, d_2 prepared *via* ^{15}N azide exchange of **4**-d_2, results in the same set of product infrared bands obtained from **4**-d_2 together with a single new band at 1552 cm^{-1}, which is assigned to ^{14}N=^{15}N stretch for $D_2N^{15}N$. Irradiation with visible light results in a decrease of all bands due to D_2NN as well as the 1552-cm^{-1} band. The 1571- and 1552-cm^{-1} bands are assigned to the ^{14}N=^{14}N and ^{14}N=^{15}N stretch of D_2NN.

In summary, H_2NN is a blue-violet species (λ_{max} 636 nm, n,π^*) with an N=N stretching frequency of 1574 cm^{-1}. This can be compared to the trans 1,2-isomer, **1**, which is yellow (λ_{max} 386 nm) with a Raman N=N stretch of 1529 cm^{-1}. At 90 °K, one thermal product from H_2NN appears to be the trans 1,2-isomer **1**.[11] The photodecomposition of H_2NN in the visible at 80 K affords H_2 and N_2.

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Bond Dissociation Energies in Ferrocene

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Cyclopentadienyl (C_5H_5) is an important ligand in organometallic chemistry, in addition to its role in forming interesting sandwich compounds, such as ferrocene, Fe(η^5-C_5H_5)$_2$. As a small, polydentate, strongly bound ligand, it is useful in producing partially unsaturated, extremely reactive species of value in modeling basic organometallic reaction chemistry, in synthesizing organometallic compounds containing particularly labile or reactive ligands, and for developing novel asymmetric ligands. Despite extensive literature on these compounds, reliable values for metal–cyclopentadienyl bond dissociation energies (BDE) are not available. The average values, which have been measured for metallocenes,[1] do not necessarily correspond to the individual bond strengths. We report here our measurements of the thermal decomposition rates of ferrocene by very low-pressure pyrolysis (VLPP) and derive the first and second bond energies.

The VLPP method has been widely used and is described in detail elsewhere.[2] The chosen gas, flowing at low pressure through a heated Knudsen cell, is heated rapidly by collisions with the walls and pyrolyzes if the temperature is high enough. The decomposition rate is measured relative to the known rate of escape into the analysis mass spectrometer. Two residence times, that is, exit aperture sizes, can be used, and gas–gas collisions are avoided at the low millitorr pressures used. Ferrocene was monitored at the parent peak (*m*/*e* 186 amu) relative to the signal level when the flow bypassed the heated reactor. Temperatures were measured by thermocouples.

The results are shown in Figure 1. Several observations indicate that decomposition is not wall catalyzed. Data taken both increasing and then decreasing the temperature, and data with carbon coated or bare quartz reactor walls, show no disparity. When the temperature is lowered below 1120 K after a run, no decomposition is observed. Thus, these rates represent the homogeneous gas-phase decomposition of ferrocene. We note, however, the prolonged exposure of the walls to ferrocene at high temperature does produce a catalytic wall coating. Attempts to perform a similar experiment for nickelocene produced rapid catalytic decomposition near 800 K. This was previously observed by Hedaya.[3]

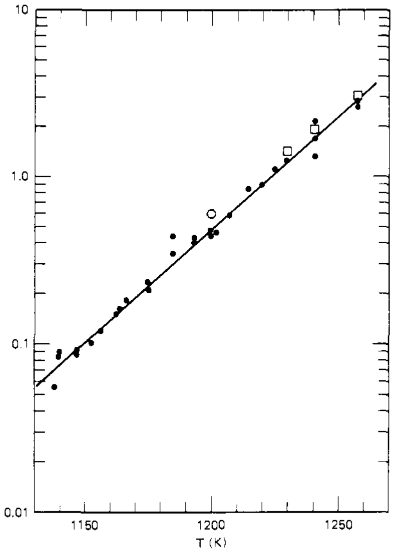

Figure 1. Very low-pressure pyrolysis data for ferrocene decomposition. Dots are small aperture, squares are large aperture. The line is the calculated fit, including falloff for log $k_\infty = 16.34 - (91.4/2.3RT)$. The open circle is the fit for a higher A factor as described in the text.

A least-squares Arrhenius fit of the data gives log A = 15.5 and E_a = 86.8 kcal/mol. However, the fact that the reaction is slightly in the falloff regime where energy-transfer collisions with the walls partially contribute to the rate must be taken into account. We have utilized a reduced Kassel formalism developed by Troe[4] which reproduces the results of full RRKM calculations. The rate constant is expressed as a correction to the Lindemann–Hinshelwood model:

$$\log k = \log (k_0/(1 + (k_0/k_\infty))) + \log F/(1 + (\log k_0/k_\infty)^2)$$

Here, k_0 is the known strong collision rate with the walls,[2] k_∞ is calculated from assumed Arrhenius parameters which we are attempting to derive via the fit, and F is calculated[4] from E_a and the ferrocene vibrational frequencies.[5] The fit shown in Figure 1 is for log A = 16.34 ± 0.54 and E_a = 91.4 ± 3.0 kcal/mol. The degree of falloff, k/k_∞, ranges from ~0.88 at 1150 K to ~0.75 at 1250 K. In general, it is not possible to uniquely determine both A and E_a from VLPP data, hence the range of values. An increase in both A and E_a is partially compensated for by an increase in the falloff and its temperature dependence. Thus, this value of E_a represents a minimum for scission of the first cyclopentadienyl ligand from ferrocene. Much larger values of A and E_a, however, are unilkely, since the fit in Figure 1 will show curvature not evident in the data when this is attempted. For example, using log A = 17.5 and E_a = 97.5 kcal/mol, we fit the data as before at 1150 and 1250 K, but the fit at 1200 K, shown in Figure 1 as the open circle, is clearly above the data.

In an attempt to resolve this ambiguity further, a laser pyrolysis experiment was undertaken at higher temperature. Experimental details are given in a recent paper on metal–carbonyl bond energies.[6] A mixture of 100 torr N_2 bath gas, SF_6 absorber, and

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traces of unimolecular reactants is irradiated by a pulsed-CO$_2$ laser. After rapid energy-transfer collisions with the excited SF$_6$, the mixture is heated to temperatures up to 1600 K. Unimolecular decomposition reactions occur, but are quenched after $\sim$10 μs when expansion cooling occurs. Yields are determined by mass spectrometric sampling of reactants from a slow flow. Here we used *tert*-butyl alcohol with known decomposition parameters,[7] as a temperature standard, monitored at m/e 57. The observed kt of 1.05 per laser shot within the irradiated volume corresponds to a 1600 K temperature. The ferrocene yield was 0.077, or $k = 7.7 \times 10^3$ s^{-1}. The VLPP Arrhenius parameters of log A = 16.34 and E_a = 91.4 kcal/mol give k_∞(1600 K) = 8.6×10^3 s^{-1} and with a pressure falloff calculation predict $k = 7.0 \times 10^3$ s^{-1}, in good agreement with the experiment. The high Arrhenius parameters, however, predict a significantly higher rate than observed: 1.45×10^4 s^{-1}, including falloff. Thus, the laser pyrolysis experiment confirms the 91.4 ± 3.0 kcal/mol VLPP activation energy.

Finally, we must convert E_a to ΔH (and then to $\Delta H(298)$), the BDE. This correction is small for a transition state featuring low vibrational frequencies ($\sim$0.5 kcal/mol), giving a BDE value of 91 ± 3 kcal/mol. The use of this kinetic value to derive a thermodynamic one assumes, of course, that there is no additional barrier to decomposition. This analysis also assumes dissociation is a simple one-step process—for example, that CpFe(η^3-C$_5$H$_5$) is not an intermediate. The high activation energy and typical A factor support a single-step mechanism.

Given the average bond energy,[1] we can then derive the second BDE, D_{298}(Fe–Cp) = 51 kcal/mol, again assuming the first dissociation does not produce electronically or vibrationally excited product. (In one sense, this is a lower limit). Given this second bond energy, FeCp should be stable and potentially functional as a catalyst below $\sim$550 K.

For comparison purposes, a bond energy for nickelocene can be derived from mass spectrometric ionization and appearance potential measurements.[3] The value of 103 kcal/mol leaves[1] a second bond energy of only 15 kcal/mol, which is highly unlikely since NiCp can be observed at 800 K. While this suggests the first ligand is the more strongly bound in this case also, the probable errors encountered with this method are evident. The 91 kcal/mol bond energy in ferrocene for the η^5-cyclopentadienyl system to iron can also be compared to the η^2-ethylene system in Fe(CO)$_4$C$_2$H$_4$, where D = 37.2 kcal/mol.[6] This difference of 2.5 times is reasonable when one compares the bonding, although the exact multiplicative factor may be fortuitous. The olefin bond[8] consists of a dative bond between the π electrons and an empty metal d orbital plus the back-bond of the π^* orbital with metal d electrons. Ferrocene has three π orbitals per ring for bonding to the metal plus back-bonding through two π^* oribtals.

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Registry No. Ferrocene, 102-54-5.

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Book Reviews

Transport in the Life Sciences. Volume 5. Cell ATP. By William A. Bridger and J. Frank Henderson (University of Alberta). John Wiley and Sons, New York. 1983. x + 170 pp. $59.95.

Considering the diversity and number of reactions in which ATP participates, one would expect a reference monograph dealing with the structure, function, and metabolism of ATP to be large and unwieldy. This monograph has neither of these characteristics. Rather than presenting a comprehensive review of the subject matter, the authors offer a concise, well-written overview, which is divided into two parts. Following a brief historical introduction, Part I, written by Dr. Bridger, is made up of four chapters (65 pages) which deal with ATP as the energy currency of the cell. Part II, written by Dr. Henderson, is comprised of five chapters (97 pages) which are more or less a review of purine nucleotide metabolism with emphasis on the biosynthesis and catabolism of ATP.

The topics presented in Part I include the thermodynamics of ATP hydrolysis, the coordination of metal ions by ATP including the tabulation of ^{31}P NMR parameters, a discussion of the reaction mechanisms of the enzymes involved in the phosphorylation of ADP to form ATP, profiles of the structure–function relationships of selected enzymes which hydrolyze ATP, and the involvement of ATP in metabolic regulation.

The topics covered in Part II are as follows: the pathways of de novo purine biosynthesis; the synthesis of adenine nucleotides directly from adenine and adenosine; the conversion of other purine bases, nucleosides, and nucleotides into adenine nucleotides; the catabolic pathways for ATP, and special pathways for the utilization of the adenosine moiety of ATP in animal cells. Each of the above topics is discussed with due consideration of individual enzymes of the pathways and factors which regulate the pathways. Topics also considered in Part II are as follows: disease states which influence ATP concentrations, most of which are the consequence of inborn errors, and drugs which affect the levels of cellular ATP.

This book is Volume 5 in the series "Transport in the Life Sciences", edited by E. Edward Bittar, and is compatible with the general theme of the series. The two overviews presented on ATP should prove to be valuable supplemental reading for undergraduate, graduate, and medical students taking courses in biochemistry and cell biology. Therefore, it would be appropriate to cite this monograph in chapters on ATP as energy currency of the cell and on purine nucleotide metabolism in introductory texts of biochemistry and cell biology.

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Solid Electrolytes. By E. C. Subbarao (Indian Institute of Technology). Plenum Press Publishers, New York and London. 1980. xvi + 298 pp. $35.00.

This book was written for scientists and engineers who are involved in the study of solid electrolytes and their applications. There appears to be a reasonable balance between fundamental studies and practical aspects. A large number of compounds are discussed including zirconia- and thoria-type solid electrolytes and the newer types such as fluorides, β-aluminas, and silver ion conductors.

The initial chapter deals with the principles of defects in ionic solids as well as the structure and properties of important solid electrolytes. Other chapters deal with the experimental problems associated with the use of solid electrolytes for a variety of measurements. There is a considerable emphasis on the thermodynamic studies which have been carried out on binary and ternary alloys and intermetallic compounds with use of oxide and fluoride solid electrolytes. Included also are corre-