results of our SCF-Xα-SW MO calculation for C_{6v}, (η^6-C_6H_6)V, summarized in Figure 2. In this description one finds (i) the degenerate $1e_{1g}$ π-level of benzene, stabilized mainly by interaction with valence $d_{xz,yz}$ orbitals on V and with negligible contributions in the $5a_1$ level from V s and p valence orbitals, giving rise formally to two strong V-C_6H_6 bonding levels housing four electrons $5a_1{}^24e_1{}^4$, (ii) two V valence orbitals d_{z^2} and d_{xy} remaining essentially metal localized with a small bonding contribution from the $d_{x^2-y^2}$ symmetry set and containing five electrons $3e_2{}^46a_1{}^1$, and (iii) three empty low-lying V–C_6H_6 antibonding orbitals $5e_1(d_{xz,yz})$ and $7a_1(s, d_{z^2})$. Overall, this scheme results in a $^2A_1$ ground electronic state for (η^6-C_6H_6)V with an orbital picture and bonding scheme essentially the same as that of the $^2A_{1g}$ ground-state parent (η^6-C_6H_6)$_2$V sandwich. Finally, the Xα transition-state calculations favor a $3e_2{}^46a_1{}^1 \rightarrow 3e_2{}^46a_1{}^04e_2{}^1$ mainly metal-to-ligand charge-transfer assignment for the 550-nm absorption of (η^6-C_6H_6)V as indicated in Figure 2.

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Registry No. (C_6H_6)V, 61332-91-0; V, 7440-62-2; C_6H_6, 71-43-2.

Direct Heterolysis of a Very Weak Carbon–Carbon Bond to a Carbocation and Carbanion

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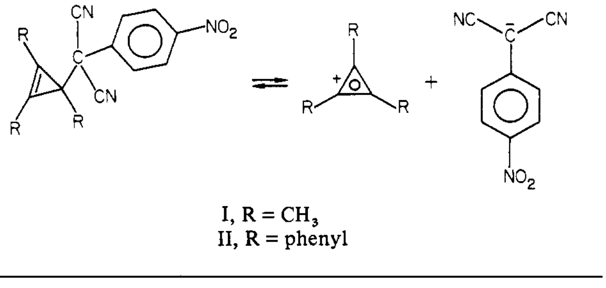
Carbocations and carbanions are the two most important types of ionic species in organic chemistry. Most discussions of organic reaction mechanisms have revolved around the effects of structural change on the thermodynamic or kinetic stability of these species or of transition states that are presumed to be close to them in energy. The simplest of polar reactions to form carbon–carbon bonds should be those involving the direct coordination of carbocations with carbanions since wide variation of the structure of both species should be possible and no allowance need be made for the involvement of leaving groups or catalysts. Correspondingly, the direct heterolysis of carbon–carbon bonds to form the two types of carbon ions should offer similar advantage. Although most carbocations and carbanions are too unstable to coexist in the same solvent, we have shown in a recent communication[1] that, with sufficient stabilization of both species, the coordination reaction can be slowed to the point where kinetic study is convenient or even to the point where no observable reaction takes place over a period of 6 mo at room temperature. An important goal[1] that is suggested by such a study has been to find a series of compounds for which the coordination and heterolysis reactions are so well balanced that the equilibrium between covalent and ionic species can be studied and with a measureable rate for either the coordination or heterolysis reaction. This implies the design of a series of compounds with such weak carbon-to-carbon bonds that they may be broken to form ions simply by dissolving them. Such a compound is represented by I.



I, R = CH_3
II, R = phenyl

Compound I was prepared by the reaction of trimethylcyclopropenium tetrafluoroborate with potassium (*p*-nitrophenyl)malononitrile in acetone solution. After the precipitated potassium tetrafluoroborate was removed by filtration and evaporating the solvents, the colorless product was taken up in a benzene–hexane mixture, filtered, and then cooled to produce crystals. A single-crystal X-ray analysis[2] defined the structure and solid-state conformation to be as presented in Figure 1. The crystal structure was solved by direct methods.[3] Full-matrix least-squares adjustment of atomic parameters[4] (anisotropic C, N, O; isotropic H) converged to $R^5 = 0.064$ over 1559 statistically significant reflections.[6] The results of this study reveal an unusually long bond length between the malononitrile and cyclopropane ring carbon atoms [C(1′)–C(1) 1.588 (4) Å >> C(1)–C(4) 1.485 (5) Å] as well as a lesser, but still significant, elongation in the adjacent bond to the phenyl ring [C(1′)–C(1″) 1.552 (4) Å].

Although crystals of I and their solution in diethyl ether are colorless at room temperature, the orange color of the carbanion appears at once if the crystals are dissolved in acetone or any more polar solvent. In chloroform solution at room temperature the ^{1}H NMR spectrum shows a broad signal at δ 1.88 for the carbocation, which on cooling to −50 °C resolves into two signals at δ 2.07 (6 H) and 1.29 (3 H) corresponding to the covalent product. These frequencies correspond almost exactly with those reported by Closs and Harrison[7] for trimethylcyclopropenium azide in CH_2Cl_2. Thus, the X-ray crystal structure provides unequivocal evidence for the existence of a covalent compound that on dissolution in polar solvents dissociates into a trimethylcyclopropenium cation and a (*p*-nitrophenyl)malononitrile carbanion. A quantitative investigation of the equilibrium between covalent and ionic species for this system is presently under way and will be reported later.[10]

The following results have been obtained for the equilibrium properties of the closely related triphenylcyclopropenium (*p*-nitrophenyl)malononitrile (II) system for which the ^{13}C NMR, infrared spectra, and elemental analysis confirm, by close analogy to compound I, the formation of a covalent crystalline material. Equilibrium constants for the covalent–ionic process were determined in six different solvents by monitoring the absorbance of the (*p*-nitrophenyl)malononitrile anion (λ_{max} = 475–490 nm, ϵ = 30 000). The Debye–Hückel limiting law, which is valid for compound II in acetonitrile, was used to correct[8] equilibrium constants for ionic strength effects resulting from heterolysis. In accordance with expectation, an excellent linear relation between the free energy of heterolysis, $\Delta G_{het}°$, and $1/D$ was found, as predicted by the Born equation (Figure 2).[10]

Equilibrium constants were also determined at several temperatures to yield the enthalpy of reaction both when approached by coordination of the ions ($\Delta H_{coord}° = -5.4 \pm 0.3$ kcal mol^{-1}) or as approached independently by heterolysis of the covalent compound ($\Delta H_{het}° = +5.5 \pm 0.5$ kcal mol^{-1}). As an independent check, the enthalpy of reaction of the ions was determined calorimetrically by thermometric titration of a solution of the cation into an excess of potassium (*p*-nitrophenyl)malononitrile[9] ($\Delta H_{coord}°$

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(1) Arnett, E. M.; Troughton, E. B. *Tetrahedron Lett.*, in press.

(2) Crystal data: $C_{15}H_{13}N_3O_2$, M_r267.30, triclinic, a = 7.684 (3) Å, b = 15.115 (6) Å, c = 7.248 (3) Å, α = 77.88 (1)°, β = 117.85 (1)°, γ = 106.73 (1)°, U = 710.0 Å^3, Z = 2, d_{calcd} = 1.250 g cm^{-3}, space group $P\bar{1}(C_i{}^1)$.

(3) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, J.-P. "MULTAN76, a System of Computer Programmes for the Automatic Solution of Crystal Structures"; Universities of York and Louvain, 1976.

(4) See paragraph at end of paper regarding supplementary material.

(5) $R = \sum||F_0| - |F_c||/\sum|F_0|$.

(6) Intensity data were recorded on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu Kα radiation, λ = 1.5418 Å; θ–2θ scans, θ_{max} = 67°) by use of procedures detailed elsewhere, see: Miller, R. W.; McPhail, A. T. *J. Chem. Soc., Perkin Trans. 2* 1979, 1527.

(7) Closs, G. L.; Harrison, A. M. *J. Org. Chem.* **1972**, *37*, 1051.

(8) This correction was less than 25% of K for all solvents, corresponding to a 0.15 kcal mol^{-1} change in $\Delta G_{het}°$.

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J. Am. Chem. Soc. **1983**, *105*, 6173-6174

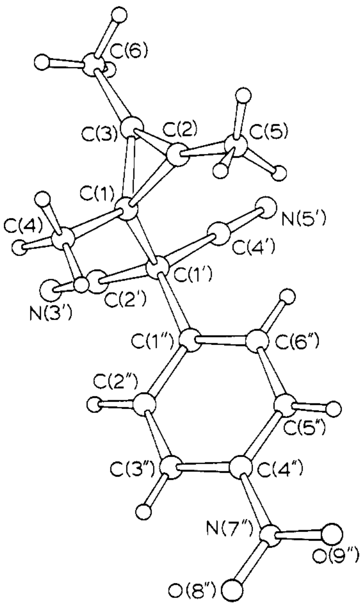

Figure 1. Structure and solid-state conformation of I.

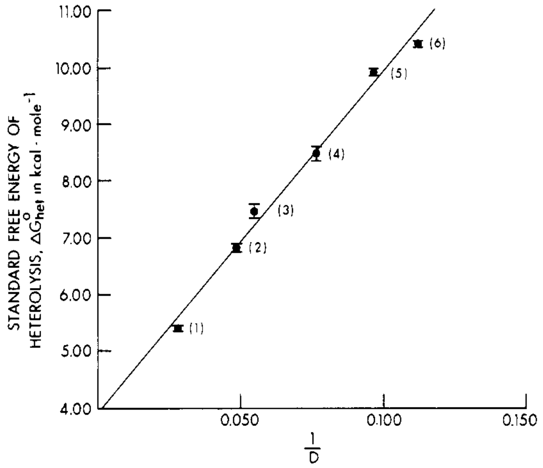

Figure 2. Born equation plot of standard free energy of heterolysis of compound II at 25 °C in six solvents of varied dielectric constant: (1) acetonitrile, (2) acetone, (3) cyclohexanone, (4) 4-methyl-2-pentanone, (5) 1,2-dichloroethane, (6) dichloromethane. Dielectric constants (*D*) are at 25 °C for 1, 2, 5, and 6 and at 20 °C for 3 and 4.

$= -6.3 \pm 0.3$ kcal mol^{-1}).

We thus report unequivocal evidence for the heterolysis of a covalent compound to produce a carbocation and a carbanion under equilibrium conditions in a variety of solvents. Subsequent articles will discuss our findings regarding the effects of structural change on the thermodynamic and kinetic properties of these processes.

Acknowledgment. We gratefully acknowledge support for this work by NSF Grant CHE-8006202.

Supplementary Material Available: Tables of atomic positional parameters and interatomic distances and angles (4 pages). Ordering information is given on any current masthead page.

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(9) The observed heat of reaction was corrected for the degree of dissociation at the final concentration (2.2 mM). We believe that the small discrepancy between the van't Hoff and calorimetric enthalpies (both in CH_3CN) results from the enthalpy term for ion pairing of $K^+BF_4^-$, which would not be detected through the temperature coefficient of the equilibrium constant for heterolysis or formation of the C–C bond.

(10) **Note Added in Proof:** The study of ΔG_{het}° for compound I has been completed by K.E.M. in the same six solvents. In acetonitrile $\Delta G_{het}^\circ = 2.76$ kcal mol^{-1} for I and the slope of the Born plot is 93.8 kcal mol^{-1} with $r = 0.997$; the corresponding values for II are 5.39 kcal mol^{-1}, 60.1 kcal mol^{-1}, and 0.995.

Electronic Ground State of Iron(II) Phthalocyanine As Determined from Accurate Diffraction Data

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The electronic ground states of iron(II) phthalocyanine (FePc) and iron(II) tetraphenylporphyrin (FeTPP) have received much attention because of their relevance to the understanding of structure–function relationships in heme proteins. While the evidence indicates that the iron atom is in an intermediate spin state in both compounds, there is considerable ambiguity concerning the spatial arrangement of the electrons. Alternative configurations that have been discussed are summarized in Table I. For FePc magnetic data and Mossbauer measurements by Dale et al.[1] have been interpreted in terms of the ${}^3E_gA$ configuration, while Barraclough et al. assume the ${}^3B_{2g}$ state to be the ground state[2] in an interpretation of their magnetic data that is partly at variance with a later crystal structure determination.[3] The ground state for FeTPP has been discussed in several articles. Goff, La Mar, and Reed report that NMR measurements support the ${}^3A_g$ ground state,[4] while Boyd et al. on the basis of magnetic measurements and a ligand field calculation conclude that the lowest state is ${}^3A_g$ followed closely by the states ${}^3E_g$ and ${}^3B_{2g}$.[5] SCF calculations by Veillard et al.[6] and by Obara and Kashiwagi[7] point to the ${}^3A_g$ state as the lowest SCF state. Nevertheless on the basis of both the calculations and the Mossbauer spectra the latter group of authors assign the ground state as ${}^3E_gA$.[7]

We have performed an accurate X-ray diffraction study of FePc at low temperature (110 ± 5 K) and refined the data with a multipole model aspherical atom formalism described elsewhere.[8] The 16709 measured reflections ($\lambda = 0.71069$ Å, $(\sin\theta)/\lambda < 1.18$ Å^{-1}) were reduced to 6733 unique intensities of which 3832 have $F^2 > 3\sigma(F^2)$, by averaging over symmetry-equivalent measurements. Conventional and multipole refinements led to $R(F)$ factors of 3.6% and 2.7%, respectively. The low-temperature structure is essentially the same as the room-temperature results described by Kirner, Dow, and Scheidt.[3] The deformation density map in the plane of the molecule (Figure 1a), defined as $\rho_{obsd} - \sum\rho_{isolated\ atoms}$, shows that density in excess of the isolated atom distribution is located along the bisectrices of the Fe–N bonds. This would not be the case for either the ${}^3B_{2g}$ or the ${}^3E_gB$ configuration (Table I), which are electron deficient in d_{xy}. A section perpendicular to the molecular plane reproduced here (Figure 1b), shows an electron-deficient area above and below the iron atom. This indicates a less-than-spherical-atom population in the d_{z^2} orbital in support of the ${}^3E_gA$ state, but at variance with the density predicted by the other remaining configuration, ${}^3A_g$.

A more quantitative assessment may be based on the experimental multipole populations from which the d-orbital occupancies can be derived.[9] The results given in the one but last column

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[†] On leave from the Institute of Biophysics, Academia Sinica, Beijing, China.

[‡] On leave from the Institute of Chemistry, Academia Sinica, Beijing, China.

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