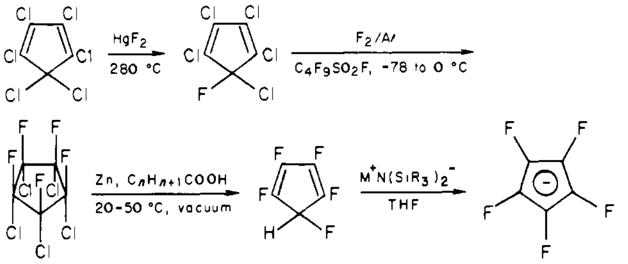
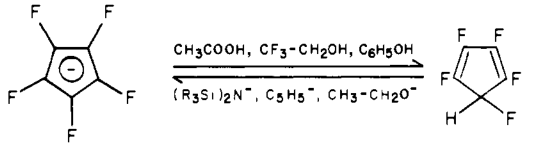
in argon and increasing temperature to give $C_5Cl_5F_5$ in one step. This wax-type material, mp 60–75 °C, is purified by a spinning band distillation, 117 °C (20 mbar), yield 49%. $C_5Cl_5F_5$ is a mixture of four isomers, as expected, which can be separated by gas chromatography. The all-cis compound shows one sharp singlet in the NMR, δ_F −121.3 ppm; the other isomers have AA'BB'C spectra as expected. Reduction of $C_5Cl_5F_5$ with zinc in medium-long carbonic acids, such as $C_6H_{13}COOH$ or $C_7H_{15}COOH$, at 10–50 °C in vacuum affords 45% of crude C_5F_5H. This 1,2,3,4,5-pentafluorocyclopentadiene is purified on a squalane/silica gel column, 55–110 °C, by gas chromatography (NMR AA'BB'CX spectra with δ_A −153.3 δ_B −162.9, δ_C −220.7, δ_H 3.8) and has to be stored at −196 °C to avoid Diels–Alder dimerization. The yield of pure material is only 22%, mainly due to losses by dimerization. The dimer $(C_5F_5H)_2$, a mixture of at least two isomers, can be converted to the monomer only at 700 °C in 5% yield (eq 1).



(1)

Metalation of the proton preferably with $M^+N(SiR_3)_2^-$ affords the title anion. THF solutions of the metal salts are unstable. The lithium salt decomposes within minutes at −110 °C, the sodium salt within hours at −78 °C, and the thallium and caesium salts at −30 °C. The $Na^+[18\text{-crown-6}]C_5F_5^-$ in THF is the most stable so far. It can be observed at 22 °C for a few hours and exhibits like the others a singlet NMR resonance at δ_F −209.0. The typical decomposition reaction is loss of metal fluoride, catalyzed especially by smaller cations, and polymerization. The instability of the metal salts and the bad crystallization behavior of crown ether complexes prevented the isolation of the pure salts so far.

The acidity of C_5F_5H has been estimated by the equilibrium eq 2, which was followed by NMR measurements. It was found



(2)

to be more acidic than cyclopentadiene (p*K*s = 15.5) but less than $CF_3–CH_2OH$ (p*K*s = 12.8).

The small effect of perfluorination on the acidity is explained by the dual effect of fluorine in aromatic systems: electron-acceptor qualities via σ bonds and donor qualities via π bonds. This is in marked contrast to 5*H*-Perfluorpentamethylcyclopentadiene, $C_5(CF_3)_5H$, which has been recently described and shows an acidity increase of about 18 orders of magnitude as compared with cyclopentadiene.[7] But this difference is conceivable since the CF_3 groups have electron-acceptor qualities only.

At present the effect of perfluorination in metallocene chemistry is unknown. We have not yet obtained any such material from C_5F_5H or $C_5F_5^-$. As seen from its acid–base behavior as compared with cyclopentadiene, it may well serve as a similar good π ligand.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Indistrie for support of this work.

---

(7) Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6633.

Ab Initio CI Study of the Hydrogen Abstraction by $NH(a^1\Delta)$

Takayuki Fueno*[1a] and Okitsugu Kajimoto[1b]

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan
and Institute for Molecular Science
Okazaki, Aichi 404, Japan

Vlasta Bonačić-Koutecký

Institut für Physikalische Chemie
Freie Universität Berlin
1000 Berlin 33, Germany

Received December 12, 1983

The NH radical as a monocentric divalent species exhibits different modes of chemical reaction, depending on its electronic state. Thus, the NH radical in the lowest singlet state ($a^1\Delta$) inserts into a covalent bond most efficiently, while the ground-state triplet ($X^3\Sigma^-$) tends to add to an unsaturated atomic center or abstract an atom from a saturated bond.[2] However, the $^1\Delta$ state can in cases manifest a radical character as well.[3] In fact, clear-cut evidence exists indicating that $NH(a^1\Delta)$ directly abstracts a hydrogen atom from paraffins to give NH_2 in a manner more or less competitive to the insertion reaction giving amines.[4] We herein wish to demonstrate theoretically how $NH(a^1\Delta)$ can enter into hydrogen abstraction reaction.

The lowest singlet state ($^1\Delta$) of NH can be represented by either a combination of two *closed-shell* configurations $(1\sigma)^2(2\sigma)^2(3\sigma)^2[(x)^2 - (y)^2)]$ or a single *open-shell* configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(x)(y)$, where x and y denote the degenerate $p\pi$-type real-function atomic orbitals (AO) orthogonal to the NH σ bond.[3,5] The two singlet states involving these leading configurations are degenerate to each other. Obviously, it is the latter configuration that is responsible to the abstraction reaction of our concern.

We have first examined

$$NH(a^1\Delta) + H_2 \rightarrow NH_2(\tilde{X}^2B_1) + H \qquad (1)$$

as a prototype of the $NH(a^1\Delta)$ abstraction reactions. The AO basis set used is the conventional split-valence 4-31G functions.[6a] For the sake of convenience, the reaction path was traced by the singlet UHF SCF geometry optimization of the entire system for fixed interatomic distances R(N–H) or r(H–H). It has been proven that the reaction proceeds, maintaining the planar $A''(C_s)$ structure throughout. The multireference double-excitation configuration-interaction (MRD-CI) calculations[7] were then conducted at several points on the SCF minimum-energy path. The configuration selection threshold T was set strictly equal to 0 μhartree to obtain the CI energy $E_{CI,T=0}$. Three-reference (3M) calculations were adopted as a standard procedure. The dimension of the configurational space used was 2678.

Figure 1 shows the change in $E_{CI,T=0}$ calculated as the function of $(r - R)$ chosen as a principal reaction coordinate. For the sake of comparison, a similar potential-energy profile calculated for the case of $NH(X^3\Sigma^-)$ is illustrated with it. For either case, we define the structure giving the maximal $E_{CI,T=0}$ value on the

---

[1] (a) Adjunct Professor at IMS for 1981–1983. (b) Present address: Faculty of General Education, University of Tokyo, Meguro, Tokyo 153, Japan.

[2] (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (b) Lwowski, W. "Nitrenes"; Wiley: New York, 1970. (c) Bader, R. W. F.; Gangi, R. A. *Chem. Phys. Lett.* **1970**, *6*, 312; *J. Am. Chem. Soc.* **1971**, *93*, 1831.

[3] Kasha, M.; Brabham, D. E. *Adv. Quantum Chem.* **1979**, *11*, 1.

[4] (a) Kajimoto, O.; Fueno, T. *Chem. Phys. Lett.* **1981**, *80*, 484. (b) Kondo, O.; Miyata, J.; Kajimoto, O.; Fueno, T. *Ibid.* **1982**, *88*, 424.

[5] Fueno, T.; Bonačić-Koutecký, V.; Koutecký, J. *J. Am. Chem. Soc.* **1983**, *105*, 5547.

[6] (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[7] Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974**, *35*, 33; **1975**, *39*, 217; *Chem. Phys.* **1975**, *9*, 75.

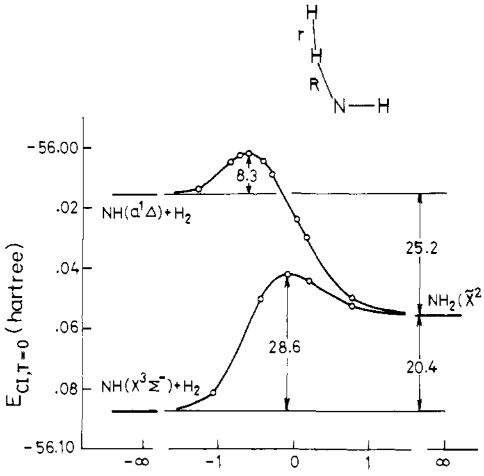


Figure 1. Potential energy profiles calculated for the reactions NH + H_2 → NH_2 + H. The energy gap values indicated are in units of kcal/mol.

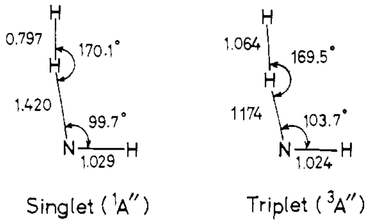


Figure 2. Geometries of the transition states (4-31G CI maxima) for the reactions NH + H_2 → NH_2 + H. Bond distances are given in units of Å.

reaction path as the transition state (TS). Geometries for the transition states thus located are shown in Figure 2. As for the geometries of NH, H_2, and NH_2, the experimental bond distances and angle have been taken from the literature.[8]

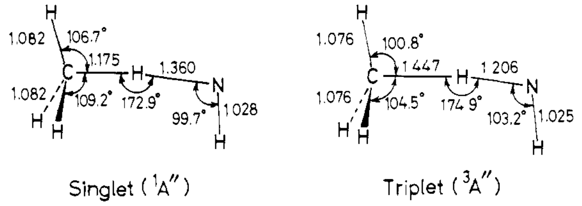
The activation barrier height $\Delta E^{\ddagger}$ calculated for the singlet reaction in question is 8.3 kcal/mol, which is considerably smaller than the value of 28.6 kcal/mol obtained previously for the corresponding triplet reaction.[5] In both cases, the square weight of the open-shell diradical configuration $(1a')^2...(4a')^2(5a')(1a'')$ contributing to the CI-expanded-state function is over 0.93 throughout the course of reaction. The energy change of reaction calculated for the singlet case $\Delta E = -25.2$ kcal/mol agrees reasonably well with the experimental heat of reaction $\Delta H^{\circ} = -26.1 \pm 3$ kcal/mol.[9,10]

The transition states, both singlet and triplet, as well as the initial and final states of reactions were subjected to the same CI calculations employing the 4-31G** basis functions.[6b] The 4-31G optimized TS geometries were adopted for these calculations. The $\Delta E^{\ddagger}$ and ΔE values obtained were 8.5 and −25.0 kcal/mol, respectively. The effects of the polarization functions have thus proved to be immaterial.

Calculations have been extended to the reaction of methane:

$$NH(a^1\Delta) + CH_4 \rightarrow NH_2(\tilde{X}^2B_1) + CH_3 \qquad (2)$$

Only the 4-31G basis set was used for the sake of computational economy. The lowest configuration-selection threshold used was $T = 10$ μhartree, and the successive four T values increasing stepwise by 10 μhartree each were adopted to obtain the extrapolated CI energy $E_{CI,T\to0}$. The transition-state geometry was searched for in exactly the same manner as for the reaction with H_2. The corresponding triplet case has also been dealt with likewise. The transition-state geometries located for both cases are illustrated in Figure 3.



Singlet (¹A″) Triplet (³A″)

Figure 3. Geometries of the transition states (4-31G CI maxima) for the reactions NH + CH_4 → NH_2 + CH_3. Bond distances are given in units of Å. The dihedral angles ϕ(HCHN) associated with the out-of-plane hydrogens are 119.5° for both the $^1A''$ and 3A″ geometries.

The activation barrier height calculated for reaction 2 is $\Delta E^{\ddagger} = 13.6$ kcal/mol (based on $E_{CI,T\to0}$), a value that is noticeably smaller than $\Delta E^{\ddagger} = 37.7$ kcal/mol obtained for a similar reaction of $NH(X^3\Sigma^-)$. The results are in line with the view[4] that the direct hydrogen abstraction from paraffins by $NH(a^1\Delta)$ in the gas phase is a fairly favorable process in the ordinary temperature region. The relatively large $\Delta E^{\ddagger}$ value obtained for the triplet case negates the possibility that the abstraction is in reality due to $NH(X^3\Sigma^-)$ formed by collisional deactivation of $NH(a^1\Delta)$.

The results of calculation presented herewith seem to serve as an endorsement of the innate capability of $NH(a^1\Delta)$ in entering into direct abstraction of a hydrogen atom from paraffins. Clearly, the radical character of $NH(a^1\Delta)$ is a natural consequence of a dominant contribution of the singlet open-shell-type configuration to its electronic structure. The situation should remain much the same in the case of the $O(^1D)$ atom allowed to react with paraffins.[11]

Acknowledgment. We are grateful to Professor R. J. Buenker for supplying the MRD-CI program. Partial support of this work by the Ministry of Education, Japan (Grant-in-Aid 56340024) is also acknowledged.

Registry No. NH radical, 13774-92-0; H_2, 1333-74-0; CH_4, 74-82-8.

---

(8) Herzberg, G. "Molecular Spectra and Molecular Structure. III. Electronic Spectra of Polyatomic Molecules"; Van Nostrand: New York, 1966. (b) Huber, K. P.; Herzberg, G. "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules"; Van Nostrand: New York, 1979.

(9) Calculated on the basis of the experimental heat of formation $\Delta H_f^{\circ} = 3.65 \pm 0.10$ eV for $NH(X^3\Sigma^-)$: Piper, L. G. *J. Chem. Phys.* **1980**, *72*, 1303.

(10) The heat of reaction was calculated from the relevant data for the heats of formation: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(11) Yamazaki, H.; Cvetanović, R. J. *J. Chem. Phys.* **1964**, *41*, 3703.

Selective Enhancement of Tyrosine and Tryptophan Resonance Raman Spectra via Ultraviolet Laser Excitation

Richard P. Rava and Thomas G. Spiro*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received March 14, 1984

The advent of pulsed lasers, capable of generating large photon fluxes in the ultraviolet region, has sparked interest in UV resonance Raman (RR) spectroscopy. In view of the importance of UV chromophores in biology, especially nucleic acid bases, and protein aromatic side chains, the UV RR technique is particularly attractive for biological applications. The technique provides selective enhancement of chromophore vibrational modes and is therefore a discriminating probe of local structure. Ziegler and Hudson have recently reported UV RR spectra of benzene[1] and alkylbenzenes,[2] excited with 212.8-nm radiation obtained by generating the fifth harmonic of the fundamental frequency (1064 nm) of the Nd:YAG laser, which are instructive with respect to the mechanism of vibronic scattering from the forbidden π–π^*

---

(1) Ziegler, L. D.; Hudson, B. *J. Chem. Phys.* **1981**, *74*, 982.

(2) Ziegler, L. D.; Hudson, B. S. *J. Chem. Phys.* **1983**, *79*, 1134.

0002-7863/84/1506-4062$01.50/0