1922 *J. Org. Chem.* **1999,** *64,* 1922−1924

Intramolecular Aromatic 1,5-Hydrogen Transfer in Free Radical Systems

T. L. Sordo*,† and J. J. Dannenberg*

Department of Chemistry, City University of New York—Hunter College and The Graduate School,
695 Park Avenue, New York, New York 10021

Received September 28, 1998

Molecular orbital calculations of the hydrogen-atom transfer between the ortho positions of the rings of the *o*-benzophenone predict an activation free energy of 8.5 kcal/mol at 298 K. Using transition-state theory, the predicted rate of H-transfer is 7.9×10^6 mol^{-1}, or 4.0×10^{-6} mol $^{-1}$, per ortho hydrogen, in excellent agreement with experimental reports. A similar H-transfer in the divinyl ketone radical is predicted to have a higher barrier by 1.4 kcal/mol despite the fact that the latter can more easily accommodate a wider C−H−C (142.3° vs 135.2°) angle in the transition state. Critical stabilization it the TS for the benzophenone radical H-transfer appears to be the result of C−H···O H-bonding interactions between the oxygen and the ortho H's that are not involved in the H-transfer. These results are confirmed by the H···O distances and the overlap populations between the H and O orbitals.

Many aliphatic carbon-centered free radicals undergo intramolecular 1,5-hydrogen migration to rearrange to isomeric structures.[1]However, aromatic 1,5-hydrogen transfer is less common.[2] Nevertheless, Karady et al. have recently reported that it plays an important role in a series of reactions of substituted benzophenone radicals generated from the corresponding diazonium salts.[3] The intramolecular 1,5-hydrogen transfer was clearly shown to take place from one ring to the other in the Pschorr cyclization, in the Sandmeyer reaction, and in hydro-, hydroxy-, and iododediazoniation reactions of substituted benzophenones. An upper limit to the rate constant for the 1,5-hydrogen shift has been reported[3] to be 10^6−10^7 s^{-1}. This H-migration seems unusually fast considering that the $\Delta H^{\ddagger}$ for H-transfer between $CH_3^{\bullet}$ and CH_4 is 14.9 kcal/mol.[4] While H-transfer between sp^2-hybridized carbons has not been extensively studied, there is not an a priori reason to expect the intrinsic barrier for these transfers to be significantly lower than for transfer between sp^3-hybridized carbons. Some chemists expect the activation energy for H-atom transfer to increase substantially if the C−H−C angle cannot attain 180°. However, we have already shown that the activation energies for such transfers are insensitive to deviations of up to 35° from linearity, but increase substantially with further deviations.[5]

In this paper, we report a comparative density functional theory (DFT) theoretical study of the mechanism of 1,5-hydrogen shift in benzophenone radical and in divinyl ketone radical. As the divinyl ketone radical was studied for the purpose of comparison, we have not explicitly considered those conformations that would not be analogous to those attainable by the benzophenone radical.[6]

Methods

We performed the DFT calculations using the B3PW91 hybrid functional. This method combines Becke's 3-parameter functional[7] with the nonlocal correlation provided by the Perdew−Wang expression.[8] According to recent reports,[9] only hybrid functionals can provide accurate description for the systems with hydrogen bonds. Since the H···C interaction that occurs along the reaction path might bear some resemblance to an H-bonding interaction, we deemed it appropriate to use this type of functional. Like the BLYP functional,[10] B3PW91 should practically eliminate the large spin contamination generally encountered using unrestricted Hartree−Fock (UHF) wave functions. Stable structures were fully optimized and transition states located at the UB3PW91/6-31G(p,d) level using the GAUSSIAN 94 series of programs.[11] Standard integration grids were employed. We calculated the vibrational frequencies of all stationary points to characterize them and obtain the zero point vibrational energies (ZPVE). ΔH's, ΔS's, and ΔG's. These calculations used the harmonic oscillator,

---

† On leave from the Universidad de Oviedo, Departamento de Quimica Fisica y Analitica, 33006 Oviedo, Principado de Asturias, Spain.

[1] Beckwith, A. L.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 251.

[2] DeTar, D. F.; Relyea, D. J. *J. Am. Chem. Soc.* **1956**, *78*, 4302. Cadogan, J. I. G.; Hutchinson, H. S.; McNab, H. *Tetrahedron* **1992**, *48*, 7747.

[3] Karady, S.; Abramson, N. L.; Dolling, U.-H.; Douglas, A. W.; McManemin, J.; Marcune, B. *J. Am. Chem. Soc.* **1995**, *117*, 5425.

[4] Creak, G. A.; Dainron, F. S. *Trans. Faraday Soc.* **1962**, *58*, 326.

[5] Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 5421.

[6] The divinyl ketone radical can assume conformations where one or both of the vinyl groups are syn to the C═O group. These conformations are lower in energy than the one considered. As they are not analogous to conformations attainable by the banzophenone radical, they would be inappropriate as a starting points for comparison with the benzophenone reaction path.

[7] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

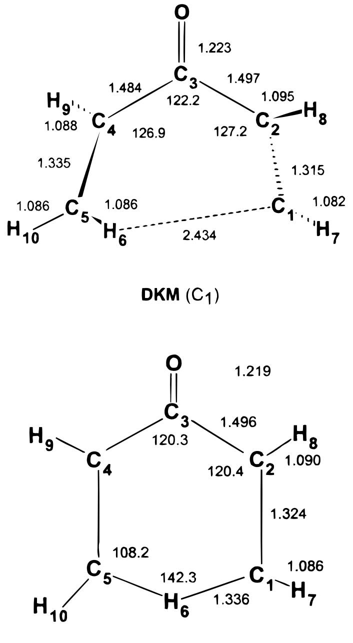
[8] Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B 45*, 13244.

[9] (a) Mamann, D. R. *Phys. Rev. B* **1997**, R10157. (b) Maerker, C.; Schleyer, P. v. R.; Liedl, K. R., Ma, T.-K., Quack, M.; Suhn, M. A. *J. Comput. Chem.* **1997**, *18*, 1695.

[10] Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Org. Chem.* **1996**, *61*, 4111. Cioslowski, J.; Liu, G.; Matinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261.

[11] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keth, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahan, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslwski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andre, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Deefres, D. J.; Baker, J.; Stewar, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94: Gaussian, Inc., Pittsburgh, PA, 1995.

10.1021/jo981961n CCC: $18.00



DKM (C_1)

DKTS (C_{2v})

Figure 1. Optimized geometries for the minimum energy structure of divinyl ketone radical (DKM) and the transition state for the 1,5-hydrogen shift (DKTS).

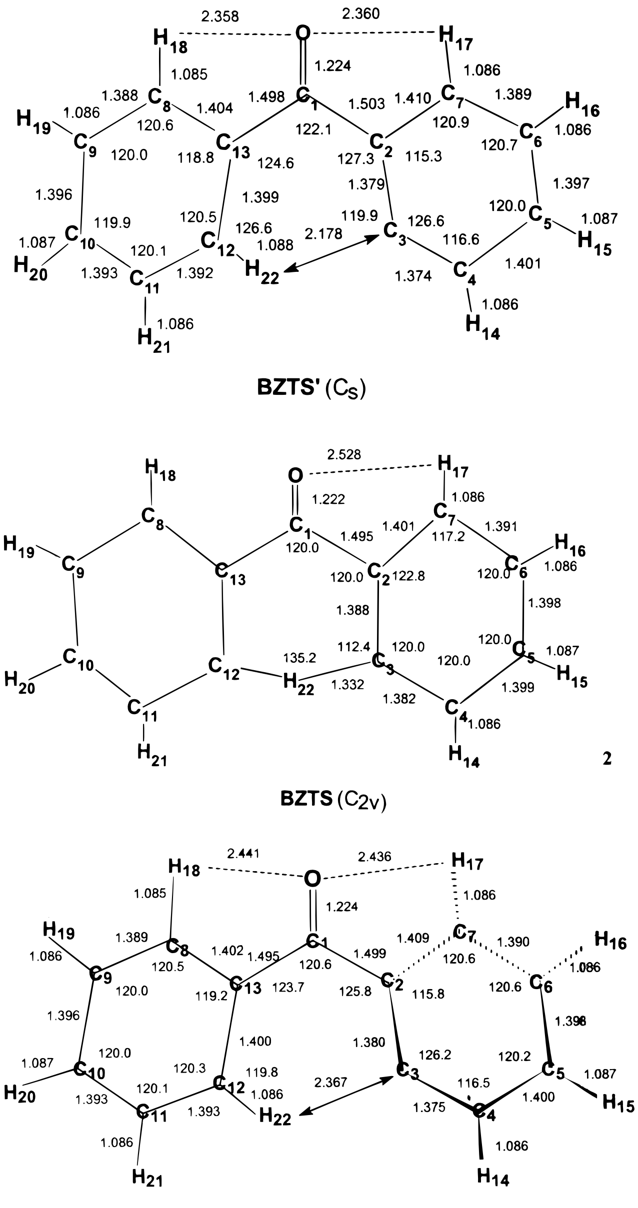
rigid rotor, and ideal gas approximations at room temperature (298.15 K) and 1 atm of pressure.

Results and Discussion

Figures1 and 2 present the optimized geometries of the critical points for the 1,5-hydrogen shift of divinyl ketone and benzophenone radicals, respectively. Table 1 displays the corresponding absolute energies, enthalpies, $\Delta H^\ddagger$, entropies, $\Delta S^\ddagger$, free energies of activation, $\Delta G^\ddagger$, and the reaction rate constant k_r evaluated through eq 1, where k, $\hbar$, and R are Boltzmann's, Planck's, and gas constants, respectively, and T is the absolute temperature.

$$k_r = \frac{kT}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \qquad (1)$$

The minimum energy structure for a conformation of the divinyl ketone radical that could be compared to the benzophenone radical[6] (DKM in Figure 1), of C_1 symmetry, has the two terminal carbon atoms C_1 and C_5 situated below and above, respectively, the plane containing O, C_2, C_3, and C_4. The migrating hydrogen atom, H_6, is bonded to C_5 and separated by a distance of 2.434 Å from C_1. The unpaired electron is formally on C_1 (spin density = 1.0635), which induces a depletion of spin population of 0.1993 in the adjacent carbon atom, C_2. The computed $\langle S^2 \rangle$ expectation value, 0.768, indicates a small spin contamination. Another conformation[6] of the radical with the C=C's syn to the C=O lies 0.4 kcal/mol lower in energy. A planar structure is 0.1 kcal/mol higher in energy. After vibrational analysis at 298 K, the planar structure is 0.5 kcal/mol lower in enthalpy, but 0.7 kcal/mol higher in free energy. The spin density of this structure is similar to that of DKM with 1.0510 on C_1 and −0.1987 on C_2.



BZTS' (C_S)

BZTS (C_{2v})

BZM (C_1)

Figure 2. Optimized geometries for the minimum energy structure of benzophenone radical (BZM), the planar transition state for the interconversion of enantiomeric radicals without H-transfer (BSTS′), and the transition state for the 1,5-hydrogen shift (BZTS).

Table 1. Total Energies, ActivationParameters, and Derived Rate Constants at 298 K

	E_{total} (hartree)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (cal/mol·deg)	$\Delta G^\ddagger$ (kcall/mol)	k_r (s^{-1})
	Divinyl Ketone Radical				
DKM	−268.5258429				
DKTS	−268.5074147	7.9	−6.7	9.9	3.4×10^5
	Benzophenone Radical				
BZM	−575.7378246				
BZMTS	−575.7210548	6.7	−5.1	8.5	7.9×10^6
BZMTS′	−575.7372494				

We located a transition state (TS) of C_{2v} symmetry, DKTS, for the 1,5-hydrogen shift in divinyl ketone radical. The migrating hydrogen atom, H_6, is equidistant (1.332 Å) from C_1 and C_5. The C_1 and C_5 atoms share the major part of the spin density (0.5767 each), with a consequent depletion of −0.1101 on each of the adjacent atoms, C_2 and C_4. This TS connects the minimum energy structure DKM with its enantiomeric conformation with an energy barrier of 11.6 kcal/mol (8.5 kcal/mol when including the ZPVE correction). The corresponding $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values (at 298 K) are 7.9 kcal/mol, −6.7 cal/(degree•mol), and 9.9 kcal/mol, respectively, leading to an absolute rate of 3.4×10^{5} s^{-1}. The computed $\langle S^2 \rangle$ value for DKTS of 0.768 again indicates low spin contamination.

Like the divinyl ketone radical, the benzophenone radical assumes a nonplanar structure of C_1 symmetry. The two rings are twisted by 22° out of the plane of the carbonyl group (see BZM in Figure 2). Distortion to a planar structure (see BZTS′ in Figure 2) requires only 0.4 kcal/mol. After vibrational correction at 298 K, the enthalpy of the planar BZTS′ is slightly less (0.4 kcal/mol) than that of BZM, but the free energy remains higher by 1.2 kcal/mol, due to the change in entropy. This planar structure represents the TS between the two enantiomeric twisted conformations of the ground-state radical. In this structure, the migrating hydrogen atom is 2.178 Å, (0.15 Å less than in planar DKM) from the carbon radical site. The ortho C−H bonds not involved in the H-transfer can either destabilize the TS due to steric repulsion with the C═O or stabilize it via H-bonding with the carbonyl oxygen. The O···H distances of 2.441 and 2.436 Å in the optimized structure decrease to 2.360 and 2.358 Å, respectively, in the planar structure. These distances are consistent with other calculated[12] and observed[13] C−H···O interactions. The Mulliken overlap populations between O and the H-bonding H's are 0.0158 and 0.0145 in the optimized radical and 0.0188 and 0.0179 in the planar structure. The unpaired electron is mostly localized on the carbon radical center (spin density = 0.9958), with very little spin on the carbon bearing the migrating hydrogen atom (0.0098) in the optimized radical. In the planar structure, the corresponding spin densities are 0.9688 and 0.0436, indicative of incremental movement along the reaction coordinate for H-transfer. The $\langle S^2 \rangle$ value obtained for this system, 0.760, indicates a small spin contamination.

We located a TS, BZTS, of C_{2v} symmetry, with the migrating hydrogen equidistant (1.332 Å) from the C atoms. As the hydrogen migrates, the two rings approach each other to facilitate the transfer. This weakens the two hydrogen bonds. The O···H distances in BZTS increase slightly to 2.528 Å, while corresponding Mulliken overlap populations decrease slightly to 0.0140. The two reacting carbon centers share most of the spin density (0.5554, each). The bridged hydrogen atom has a negative spin density of 0.1036. BZTS connects two equivalent BZM structures with an energy barrier of 10.52 kcal/mol. The $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$ values are 6.7 and 8.5 kcal/mol and −5.1 cal/mol•deg, respectively. The $\langle S^2 \rangle$ value obtained in this case is 0.762, again displaying small spin contamination. The free energy of activation leads to a predicted rate constant of 7.9×10^{6} s^{-1}, after applying a statistical factor of 2 (as there are two equivalent ortho H's that can migrate). This value is in good agreement with the experimental[3] upper limit of $10^{6}-10^{7}$ s^{-1}. In the experimental work, only one of the ortho positions had an H that could migrate. Thus, the statistical factor of 2 would not apply. The predicted k_r would then be 4.0×10^{6} s^{-1}.

The lower barrier for the benzophenone reaction seems due to the stabilization of the planar structure by the two C−H···O interactions and the greater extent of spin delocalization in BZTS compared to DKTS. The C−H···O interactions turn a potentially repulsive into an attractive interaction. This allows the radical to easily assume a planar conformation, facilitating passage to the TS. Such interactions are typically about 1 kcal/mol each, which is consistent with the difference in the potential energy barrier of about 1.5 kcal/mol (as some of the H-bonding stabilization will be sacrificed to the planarization energy of the radical) and the consequent decrease in the distance between the migrating H-atom and the radical center.

A comparison of the structures of the two TS's is instructive. The C−H−C angle for DKTS is 142.3°, while that for BZTS is 135.2°. These represent distortions of 37.7° and 44.8° from linearity, respectively. According to an earlier study, we would expect a difference in activation enthalpy of slightly less than 1 kcal/mol simply on this difference in C−H−C angle.[5] Based upon this angle alone, the relative activation energy for the divinyl radical should be lower by this amount. Thus, the C−H···O interactions and spin delocalization might play larger roles than originally apparent, as they must overcome this expected activation difference. The DKTS structure can accommodate a smaller C−H−C angle as the terminal CH_2 group is more free to bend its valence angle than the analogous carbon in the phenyl ring (to which it is tethered) of a benzophenone radical. Thus the C−C−H angle in DKTS is 108.2°, while that in BZTS is 112.4°.

The effect of tunneling must be considered in H-transfers of this sort. Normally, tunneling would be either incorporated in the preexponential factor of the Arrhenius equation or incorporated into the transmission coefficient of transition-state theory.[14] It would become relatively more important at low temperatures, where traversing the activation barrier would become less facile. This could result in a deviation form linearity in an Arrhenius plot at low temperatures. No appreciable deviation was noted in the experimental study of H-transfer from methane to methyl radical.[4]

In summary, DFT/UB3PW91 calculations render electronic wave functions only slightly spin contaminated, allowing meaningful calculations to be performed. Using such calculations can accurately predict the value of the rate constant for 1,5-hydrogen shift in benzophenone radicals. A comparative analysis of this hydrogen migration with that in the divinyl ketone radical clearly shows that the very favorable dynamics of this process in the aromatic system is a consequence of the planarity of the benzophenone radical owing to the presence of a double intramolecular hydrogen bond coupled with somewhat increased spin delocalization.

Acknowledgment. T.L.S. is grateful to the Department of Chemistry of the Hunter College of the City University of New York for warm hospitality and DGICYT (Spain) for financial support (PB94-1314-C03-01).

JO981961N

---

[12] Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 7903. Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 12197. Turi, L.; Dannenberg, J. J. *Chem. Mater.* **1994**, *6*, 1313.

[13] Peterson, K. I.; Klemperer, W. J., *J. Chem. Phys.* **1984**, *81*, 3482. Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

[14] Schatz, G. C. *Chem. Rev.* **1987**, *87*, 81.