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Gas Phase Carbon and Deuterium Isotope Effects on Electron Affinity of Benzophenone: A Combined Experimental and Theoretical Study

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Abstract: Carbonyl-^{13}C, ^{17}O, and C_6D_5 isotope effects (IEs) on the electron transfer equilibrium between benzophenone and benzophenone radical anion were determined by means of fourier transfer ion cyclotron resonance (FT-ICR) measurements and the ab initio MO calculations (UHF/6-31G*). The experimental and theoretical IEs are in excellent agreement with each other ($K_{12}/K_{13} = 1.03$ (50 °C, ICR), 1.026 (50 °C, MO) and $K_{D5}/K_{H5} = 1.35$ (50 °C, ICR), 1.325 (50 °C, MO)). The carbonyl-^{13}C, ^{17}O, ring $^{13}C_{12}$, and D_{10} IEs were calculated as 1.044, 1.025, 1.206, and 2.812, respectively, at −75 °C. The carbonyl-^{13}C and ^{17}O IEs disagree with the reported IEs in liquid NH_3 ($K_{12}/K_{13} = 2.0$, $K_{16}/K_{17} = 0.26$, at −75 °C, Stevenson et al. *J. Phys. Chem.* **1988**, *92*, 3687) and are close to unity as generally expected. The present results do not support the explanation in terms of an ion association effect in the liquid phase.

In a series of papers, Stevenson and co-workers reported equilibrium isotope effects (IEs) on electron transfer (ET) between aromatic compounds and their radical anions in solution (eq 1 for example).[1−5] The claimed large heavy atom IEs were questioned by Wolfsberg, who carried out IE calculations based on the statistical mechanical theory and the cut-off procedure[6] with estimated force constants and showed that the heavy atom IEs should be close to unity.[7] Later, Stevenson et al. carried out additional experiments with both EPR measurements and physical separation of the anion radical species from the neutral molecules and reported that they confirmed the earlier results.[8,9] They explained the discrepancy between experiment and theory in terms of the difference between the gas phase and solution; it was assumed that in solution a counter cation (Na^+ or K^+) interacts with the radical anion, making IEs far from unity.[5] Quite recently, however, Holm reported that K_{eq} in eq 1 is close to unity as indicated by Wolfsberg.[10]

Kinetic IEs are one of the most useful criteria in mechanistic studies of organic reactions.[11,12] We have used carbonyl-carbon kinetic IEs as a mechanistic probe in relation to a possible involvement of the ET process in nucleophilic addition reactions of benzophenone and benzaldehyde.[13] The size of the equilibrium IE for the ET processes is critical for the use of the kinetic IEs for mechanistic study. Therefore, we determined the intrinsic equilibrium IEs for ET to benzophenone by means of an ICR experiment and ab initio MO calculations. The results showed that the heavy atom equilibrium IEs are close to unity and that the reported discrepancy cannot be rationalized by the reason mentioned above.

The equilibrium IEs for the ET process to benzophenone/2,3,4,5,6-D_5 benzophenone and to carbonyl-^{13}C benzophenone/2,3,4,5,6-D_5 benzophenone were measured at 50 °C by fourier transfer-ICR mass spectrometry.[14,15] Since benzophenone and ^{13}C benzophenone differ by only one mass unit and also because the equilibrium IE was close to unity, the results for the competition between benzophenone and ^{13}C benzophenone were less reliable than other cases. The ^{13}C equilibrium IE was then computed from the results of benzophenone/D_5 benzophenone and ^{13}C benzophenone/D_5 benzophenone. The observed equilibrium IEs are listed in Table 1 together with those reported by Stevenson and Holm.

Ab initio calculations were carried out for benzophenone and benzophenone radical anion at the UHF/6-31+G* level[16] by using Gaussian 92.[17] Equilibrium IEs were calculated according to Bigeleisen's equation (eq 2)[18] from the ab initio vibrational frequencies with the scaling factor of 1.12 for overestimation

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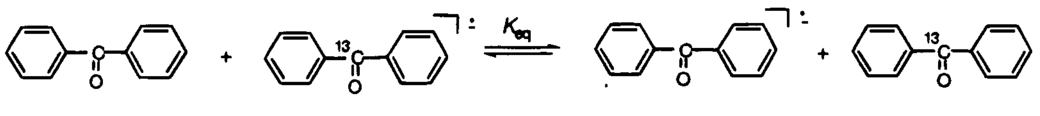

(1)

K_{eq} = 2.0 at -75 °C

Table 1. Experimental and Theoretical Equilibrium Isotope Effects for Electron Transfer Processes to Labeled Benzophenone

		ab initio calculations			EPR method[c]		separation method[c]		
labeled position	ICR method 50 °C	50 °C	25 °C	−75 °C	25 °C	−75 °C	0 °C	25 °C	−75 °C
$^{13}C{=}O$	1.01 ± 0.02[a]	1.026	1.028	1.044	1.72 ± 0.12[d,e]	2.00 ± 0.24[f]	1.021 ± 0.013[h]		
D_5	1.35 ± 0.02[b]	1.325	1.370	1.671					
D_{10}		1.762	1.877	2.812		1.92 ± 0.15[g]	1.064 ± 0.008[h]	1.75 ± 0.12[d]	
$C{=}^{17}O$		1.014	1.016	1.025		0.26 ± 0.02[f]			
$^{13}C_{12}$		1.113	1.125	1.206					1.20 ± 0.06[g]

[a] Calculated from $D_5/^{12}C$ and $D_5/^{13}C$ (1.31 ± 0.02, $n = 7$). [b] Direct measurements. Average of six determinations. Errors are the standard deviations. [c] Data determined in liquid NH_3 unless otherwise noted. [d] Taken from ref 4. [e] In HMPA [f] Taken from ref 5. [g] Taken from ref 8. [h] Taken from ref 10.

Table 2. Electron Transfer Equilbrium Constants[a]

run	abundances of neutrals[b] $[BP(D_5)]/[BP(^{12}C)]$	$K(^{12}C/D_5)$	run	abundances of neutrals[b] $[BP(D_5)]/[BP(^{13}C)]$	$K(^{13}C/D_5)$
1	0.249	1.35_1	1	0.404	1.32_6
2	0.545	1.39_1	2	0.480	1.33_5
3	0.651	1.32_3	3	0.600	1.28_7
4	0.863	1.33_8	4	0.806	1.28_7
5	1.011	1.36_3	5	1.014	1.28_4
6	1.156	1.33_5	6	1.356	1.29_7
			7	1.798	1.33_1
	mean value	1.35_0		mean value	1.30_6
	standard deviation	0.02		standard deviation	0.02

[a] At 50 °C. [b] Determined from relative intensities of molecular ion recorded on FT mass spectrometer under positive ion mode.

of the HF frequencies. Here *u* stands for *hν*/*kT*, subscript 1

$$\frac{k_1}{k_2} = \left[\frac{3n-6}{\prod_i}\right]\left(\frac{u_{1i*}}{u_{2i*}} \times \frac{e^{-u_i*/2}}{e^{-u_2*/2}} \times \frac{1-e^{-u_i*/2}}{1-e^{-u_2*/2}}\right)\frac{3n-6}{\prod_i}\left(\frac{u_{2i}}{u_{1i}} \times \frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}} \times \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}\right) \quad (2)$$

and 2 refer to normal and labeled isotopes, respectively, and superscript * means radical anion species. Calculated IEs at 50 °C (temperature at which the ICR experiment was done) and at −75 °C and 25 °C (temperatures at which previous measurements were done) are listed in Table 1. The theoretical IEs in the gas phase are in excellent agreement with the ICR data wherever the comparison can be made, which indicates that the numbers obtained by the ab initio calculations are good estimates of the gas phase IEs.

The present results disagree with those reported by Stevenson and co-workers in most cases (Table 1). Their IEs are too large either in the normal direction (2.00 vs 1.044, for $^{13}C{=}O$) or in the inverse direction (0.26 vs 1.025, for $C{=}^{17}O$) compared to those determined in the present study. It was suggested that Na cation forms an ionic bond with carbonyl oxygen of benzophenone radical anion; this additional bonding would make the heavy atom IEs large as observed.[5] However, large $^{13}C{=}O$ IE (1.72) was also observed in HMPA solvent,[4] although ketone radical anions were considered to be "free from ion association" in HMPA.[19] Furthermore, a recent result by Holm of $^{13}C{=}O$ IE in the liquid phase is small (1.021) and agrees well with the present gas phase value.[10] These results clearly indicate that the ion association cannot be the main reason for the discrepancy.

It is important to point out that the data determined by the separation experiment are generally in good agreement with the ICR and the ab initio results while those measured by the EPR method are not. Thus, the $^{13}C{=}O$ IE (1.021 at 0 °C),[10] the ring ^{13}C IE ($^{13}C_{12}$, 1.20 at −75 °C),[8] and the D_{10} IE (1.75 at 25 °C)[4] determined by the separation method are similar in magnitude to the ICR IE (1.03 at 50 °C, $^{13}C{=}O$) and the calculated results (1.028 at 25 °C, and 1.206 and 1.762 at −75 °C, $^{13}C{=}O$, $^{13}C_{12}$, and D_{10}, respectively). By contrast, D_{10} IE (1.92 at −75 °C)[8] determined by EPR is much smaller than the calculated value (2.812). The only exception is the D_{10} IE (1.064 at 0 °C),[10] which does not agree with the gas phase value among those determined by the separation experiment.

In summary, we showed that intrinsic carbonyl-^{13}C and ^{17}O equilibrium IEs on the ET process to benzophenone are close to unity. The reason why the reported IEs in liquid NH_3 determined by EPR are so different from these numbers is not clear. More thorough investigation is needed to solve this discrepancy.

Experimental Section

Carbonyl-^{13}C and ring D_5 labeled benzophenones were prepared from $Ba^{13}CO_3$ (Prochem, 98.5% isotopic purity) and benzene-d_6 (Merck) according to the standard procedures. All chemicals were purified by recrystallization and sublimation under vacuum to avoid contamination of high volatile impurities like solvent, and their purities were confirmed by NMR and MS spectra.

The equilibrium constants for electron-transfer reactions in the gas-phase were measured on an Extrel FTMS 2001 Fourier transform mass

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spectrometer equipped with a 3.0 T superconducting magnet. An experiment was initiated by a pulsed electron beam (electron energy of *ca.* 2–3 eV, uncorrected) through the ICR cell. Each neutral sample was separately introduced into the ICR cell through a variable leak value (ANELVA) so that the total pressure became *ca.* 10^{-6} Torr. The electron transfer equilibrium was achieved within 2 to 3 s of initiation of the reaction (depending on the pressure of neutrals), and an equilibrium constant K was calculated by using eq 3

$$K = [B^{\bullet -}][A]/[A^{\bullet -}][B] \quad (3)$$

The relative abundances of $A^{\bullet -}$ and $B^{\bullet -}$ ions were determined by relative intensities of ICR mass spectra when the equilibrium was attained. The relative abundances of the neutral molecules were determined by the relative intensities of molecular ion peaks of ICR mass spectra recorded under the positive ion mode, which was in agreement with that measured by means of a Bayard–Alpert type ionization gauge (ULVAC GI-D3). Since benzophenones investigated in this study have low vapor pressure at room temperatre, it was necessary to operate the inlet system and the ICR analyzer chamber at elevated temperatures. The sample inlet system was warmed to 70 °C with resistance heating tapes, and the ICR chamber was kept at 50 ± 1 °C. Several measurements were carried out for each electron transfer equilibrium under different relative abundances of two neutrals (Table 2).

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