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Deuterium and ^{13}C Isotope Effects on the Benzophenone Ketone/Ketyl Equilibrium

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In a series of papers, Stevenson et al. have published[1] the measurements of heavy atom isotope effects (IEs) on electron exchange equilibria between organic molecules and their anion radicals as, for example, between benzophenone and [*carbonyl*-^{13}C]benzophenone dissolved in liquid ammonia:

$$\underset{\mathrm{I}}{Ph_2CO} + \underset{\mathrm{II}}{Ph_2{}^{13}CO^-M^+} \rightleftharpoons \underset{\mathrm{III}}{Ph_2CO^-M^+} + \underset{\mathrm{IV}}{Ph_2{}^{13}CO} \qquad (1)$$

$$\frac{[\mathrm{III}][\mathrm{IV}]}{[\mathrm{I}][\mathrm{II}]} = K_1 \qquad (2)$$

Stevenson et al. gave values for K_1 of the order 2.0. In a note, Marx et al. on theoretical grounds raised doubt about the possibility of having IEs of this magnitude.[2] In a recent paper from 1993, Stevenson et al. presented new measurements, this time including experimental details.[3] The new results were in accordance with the old data.

Since the problem was therefore unsettled, mesurements were performed in this laboratory following Stevenson's preparative procedure except for the use of higher concentrations and for use of sodium instead of potassium. K_1 was determined indirectly from a comparison of the equilibria obtained using (1) benzophenone and decadeuteriobenzophenone and (2) ^{13}C-labeled benzophenone and decadeuteriobenzophenone. The analytical part of the procedure was improved by the use[4] of GC instead of quantitative ESR and mass spectroscopy. GC analysis in this case assures a maximum of accuracy, and most sources of systematical errors are eliminated because only *ratios* between GC integrals have to be obtained. Although benzophenone and perdeuteriobenzophenone show base-line separation on the GC column, they are still very close, which excludes injection discrimination and allows a reproducibility of the integral ratios of ±0.3%. [^{12}CO]- and [^{13}CO]benzophenone have identical retention times in GC.

In the experiment equimolar amounts of d_{10}-benzophenone and a test benzophenone (ca. 0.1 mM each) dissolved in 1.5 mL of liquid ammonia were reacted with a deficiency of sodium (1.6-cm sodium wire, ca. 0.1 mM, N_2 drybox) in a sealed ampule at 0 °C. After the sodium had dissolved, the mixture was kept for 15 min at 0 °C, after which the ammonia was evaporated at 0 °C, aspirator vacuum finally being applied. The remaining dark greenish-blue viscous oil was extracted with 3 mL of sodium-dried pentane, which was decanted and evaporated to give the unreacted benzophenones. The pentane-insoluble ketyl salts were treated with an excess of iodine in diethyl ether. Excess iodine and sodium iodide were removed by reaction with aqueous sodium thiosulfate. The ether was separated, washed with water, dried with magnesium sulfate, and evaporated. Total recovery of benzophenones from the two phases was above 90%. The melting point of recovered unreacted benzophenones was 46–49 °C. The melting point of benzophenones recovered from ketyl was 34–45 °C.

Table 1. Equilibrium Constants in Liquid Ammonia at 0 °C for Reaction 1, M = Na, for Isotopically Labeled Benzophenones[a]

I/II	K_1
$Ph_2CO/C_{12}D_{10}CO$	1.064 ± 0.008
$Ph_2{}^{13}CO/C_{12}D_{10}CO$	1.042 ± 0.008
$Ph_2CO/Ph_2{}^{13}CO$	1.021 ± 0.013

[a] The values given are the averages of five experiments. Standard deviations are shown.

The two fractions were analyzed by GC using a 100-m capillary column as reported.[5] Benzhydrol signals were absent, which indicated that contamination with water vapor had been avoided.

The D/H ratios were determined, and the equilibrium constant K_1 was found by dividing the D/H ratio for the unreacted ketones by the D/H ratio for the regenerated ketones according to eq 2. A total of five experiments were run, and the results are given in Table 1.

Benzophenone and ^{13}C-labeled benzophenone are found in the "ketyl phase" in concentrations respectively 6.4% and 4.2% higher than that perdeuteriobenzophenone. This means that the equilibrium constant for [^{12}CO]- and [^{13}CO]benzophenone is 1.021. The solution electron affinity of [^{12}CO]benzophenone in liquid ammonia is then 2.1% higher than that of [^{13}CO]benzophenone and not 100% higher as maintained by Stevenson et al. Since the effect of exchanging potassium with sodium must be considered marginal, the results obtained by Stevenson et al. are therefore unrealistic.

Indirect measurements of ^{13}C and ^{14}C IEs for K_1 obtained from kinetic work have indicated values of 1.000 for the lithium salt of benzophenone ketyl.[6] "Kinetic" values of K_1 for the magnesium salt have been reported from 1.007 for [^{14}CO]-benzophenone to 1.027 for [^{13}CO]benzophenone depending on reaction conditions.[5,7]

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