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The effects of t-butyl substituents on the thermodynamic stability of the cyclopentadienide ion

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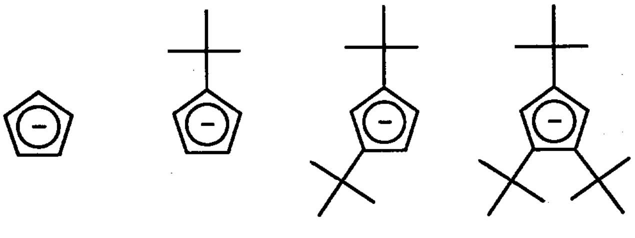
Abstract

The effects have been quantified of t-butyl substituents on the thermodynamic stability of cyclopentadienide ions with no, one, two, and three t-butyl groups, 1^-, 2^-, 3^- and 4^-, respectively. The stability estimated from oxidation potential values decreases in the order 1^- (+0.04 V) > 2^- (−0.16 V) > 3^- (−0.28 V) > 4^- (−0.45 V). The stability evaluated from pK_a values decreases in the same sequence (**1H**: 18.2, **2H**: 19.9, **3H**: 21.9, and **4H**: 25.0 in DMSO). The t-butyl substituent reduces the thermodynamic stability of cyclopentadienide ion in step with increasing number of substituents and this is most probably due to a decrease in solvation and an increase in inductive effect in the carbanion.

Key words: Butyl; Cyclopentadienide; Thermodynamics; Potassium; Lithium

Although derivatives of cyclopentadienide ion are stable 5C-6π nonbenzenoid aromatic systems, their synthesis is beset by serious problems which include susceptibility to electrophilic attacks and to oxidation, the fast dimerization reaction of their precursors, cyclopentadiene derivatives, *etc.* In order to overcome them, a bulky space-filling substituent such as the t-butyl group has been introduced as a protecting group in many cases [1]. However, the effects on the thermodynamic stability of cyclopentadienide ion of t-butyl substituents have not been evaluated. In this work, the destabilizing effects of t-butyl substituents have been quantified in terms both of the oxidation potentials (E_{ox}) for non-, mono-, di-, and tri-t-butylated cyclopentadienides (1^-, 2^-, 3^-, and 4^-, respectively; Fig. 1) and of the equilibrium acidities (pK_a) for the corresponding conjugate acids.

Compound **1H** was obtained by thermal depolymerization of dicyclopentadiene just prior to use. Preparation of **2H** was accomplished in yields of 49.0% (lit., 51% [2a], 33% [2b], and 66% [2c],) by the reaction of cyclopentadienide, 1^-, with t-butylchloride [2]. Compound **3H** was obtained in 76.2% yield (lit. [3], 90%) together with a small amount of **4H** by a phase-transfer-catalyzed alkylation of **1H** [3]. Compound **4H** was separately synthesized in 66.9% yield by $LiAlH_4$-$AlCl_3$-reduction [4] of 2,3,5-tri-t-butylcyclopentadienone which had been obtained in 35.7% yield (lit. [5], 37.3%) by the oxygenation of 2,4,6-tri-t-butylphenol [5]. Further alkylation of tri-t-butylcyclopentadienone followed by reduction and subsequent dehydration gave tetra-t-butylcyclopentadiene (**5H**) [6] in 14.0% overall yield (lit. [6], 7.8%).



1^- **2^-** **3^-** **4^-**

Fig. 1. t-Butylcyclopentadienide ions, 1^-–4^-.

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TABLE 1. ^1H and ^{13}C NMR spectral data for t-butylcyclopentadienide ions (BCPD) in THF [a]

BCPD [b]	^1H NMR		^{13}C NMR		
	CH_3	Ring-H	CH_3	$\rangle C \langle$	Ring-C
$\mathbf{1}^-$ [c]	–	5.57 [d]	–	–	102.1 [e]
$\mathbf{2}^-$ [f]	1.29 (s, 9H)	5.36 (m, 2H)	32.4 (q)	35.6 (s)	101.4 (d) 132.2 (s)
		5.42 (m, 2H)			103.8 (d)
$\mathbf{3}^-$ [g]	1.17 (s, 18H)	5.38 (s, 3H)	34.7 (q)	35.0 (s)	98.9 (d) 131.9 (s)
		5.48 (br s, 2H)			100.8 (d)
$\mathbf{4}^-$ [a]	1.10 (s, 9H)	5.56 (s, 2H)	34.8 (q)	33.5 (s)	101.5 (d) 124.6 (s)
	1.27 (s, 18H)		36.4 (q)	34.6 (s)	125.8 (s)

[a] δ; 90 MHz (^1H) and 23 MHz (^{13}C); counter cation: Li^+; in THF-d_6, unless otherwise noted. [b] $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$ and $\mathbf{4}^-$: non-, mono-, di-, and tri-t-butylated cyclopentadienide, respectively. [c] Counter cation: Na^+. [d] L.M. Jackman and S. Sternhell, *Applications of N.M.R. Spectroscopy in Organic Chemistry* Pergamon, Oxford, 1969, p. 266. [e] J.B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972, p. 91. [f] 270 MHz (^1H) and 68 MHz (^{13}C); in THF:THF-d_8 (9:1). [g] Counter cation: K^+.

Although t-butylcyclopentadienes seem to be a mixture of three or more isomers, ^{13}C NMR spectroscopy indicates the existence of two (1- and 2-substituted), three (1,3-, 1,4-, and 2,5-disubstituted), one (1,3,5-trisubstituted), and one (1,2,4,5-tetrasubstituted) isomer for **2H**, **3H**, **4H** and **5H**, respectively, as previously reported [1a,3,6]. Steric energies for these t-butylcyclopentadienes by MMP2 calculations [7*] indicate that the probabilities of existence are 79% for 2-substituted isomer and 21% for 1-substituted isomer of **2H**, 69%, 19%, and 12% for 1,3-, 1,4-, and 2,5-disubstituted isomers, respectively, of **3H**, 1,3,5-trisubstituted isomer alone for **4H**, and only 1,2,4,5-tetrasubstituted isomer for **5H**.

t-Butylcyclopentadienide ions were generated by the deprotonation of the corresponding cyclopentadienes with ^tBuOK or ^nBuLi *in vacuo* or under argon. The ^{13}C and ^1H NMR spectral data for t-butylcyclopentadienide ions are summarized in Table 1. From **5H**, however, no generation of the corresponding carbanion, $\mathbf{5}^-$, could be detected under similar reaction conditions, being due to a large increase in steric energy in the transformation.

Dynamic ^{13}C and ^1H NMR spectra (25–140°C in THF) for a mixture of each t-butylcyclopentadiene with its corresponding anion (1:1) are observed as additive spectra of those for each species to demonstrate that the rate of proton transfer reaction between these two species should be very slow on the NMR time scale.

The oxidation potentials for t-butylcyclopentadienide ions in DMSO were measured under argon by cyclic voltammetry (*vs.* Ag/Ag^+, referenced to SHE) with ferrocene as standard. Each oxidation wave was irreversible and this gave the E_{pa} value alone. The lack of reversible behaviour is due to a rapid chemical decomposition of the radicals [8] rather than electrochemical difficulties. E_{ox} (E_{pa}) values are +0.04 (lit. [9], +0.028), −0.16, −0.28, and −0.45 V for $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$, and $\mathbf{4}^-$, respectively (Table 2), and decrease linearly in the sequence with an increase in the number of t-butyl substituent ($\Delta E_{ox}/^tBu \sim -0.16_3 \pm 0.04_3$ V). Consequently, the cyclopentadienide ions become less stable to one electron oxidation reactions in the sequence, presumably resulting from steric inhibition of solvation and an increase in inductive effect in the carbanions [8].

The pK_a values of t-butylcyclopentadienes were measured in DMSO under argon by means of the UV spectral method using indicators [10], *i.e.*, 9-phenylfluorene, fluorene, and acetophenone (pK_a values 17.9, 22.6, and 24.7 [11], respectively): 18.2 (lit. [11], 18.0), 19.9, 21.9, and 25.0 for **1H**, **2H**, **3H** and **4H**, respectively (Table 2). The stability estimated from the pK_a values for the conjugate acids decreases linearly with an increasing number of t-butyl substituent groups ($\Delta pK_a/^tBu \sim 2.2_7$ ($\pm 0.8_3$)) within experimental error, presumably owing to steric inhibition of solvation and an

TABLE 2. Oxidation potentials for t-butylcyclopentadienide ions ($BCPD^-$) and equilibrium acidities and bond dissociation energies (BDE) for their conjugate acids (BCPD-H) in DMSO

BCPD [a]	E_{ox} (V) [b]	pK_a [c]	BDE (kcal/mol) [c,d]
$\mathbf{1}^-$	+0.04 (±0.01)	18.2 (±0.1) [e]	81.6 (±0.4)
	(+0.028 [f])	(18.0 [g])	(81.2 [f], 81.7 [h], 82.9 [i])
$\mathbf{2}^-$	−0.16 (±0.01)	19.9 (±0.2) [e]	79.4 (±0.6)
$\mathbf{3}^-$	−0.28 (±0.02)	21.9 (±0.3) [j]	79.5 (±1.1)
$\mathbf{4}^-$	−0.45 (±0.03)	25.0 (±0.3) [k]	79.8 (±0.9)

[a] $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$ and $\mathbf{4}^-$: non-, mono-, di-, and tri-t-butylated cyclopentadienide, respectively; counter cation: K^+. [b] *vs.* Ag/Ag^+, referenced to SHE, with ferrocene as a standard. [c] For the corresponding conjugate acids (BCPD-H). [d] $BDE = 1.37 \cdot pK_a + 23.1 \cdot E_{ox} + 55.9$ (ref. 11). [e] Indicator: 9-phenylfluorene (pK_a: 17.9 (ref. 11)). [f] Cited from ref. 12. [g] Cited from ref. 11. [h] Cited from ref. 9. [i] Cited from ref. 13. [j] Indicator: fluorene (pK_a: 22.6 (ref. 11)). [k] Indicator: acetophenone (pK_a: 24.7 (ref. 11)).

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* Reference number with an asterisk indicates a note in the list of references.

increase in inductive effect in the carbanions [8] similar to the case of E_{ox} as mentioned above. The extent of the destabilization of cyclopentadienide ion by one t-butyl substituent is almost the same as that observed with the fluorenide ion (9-substituted) [12]. On the other hand, in contrast to the t-butylcyclopentadienide ions, phenylcyclopentadienide ions become more stable along with an increase in number of the substituent. However, the stability is not proportional to the number of substituents because all (probably more than two) phenyl rings are unable to be coplanar with the cyclopentadienide ring because of the steric hindrance.

A linear relationship, $E_{ox} = 16.5 - 0.788 \cdot pK_a$ ($r = 0.935$), can be found for t-butylcyclopentadienides and the other hydrocarbon carbanions including pentamethyl- and pentaphenylcyclopentadienides [11]. Bond dissociation energies ($\text{BDE} = 1.37 \cdot pK_a + 23.1 \cdot E_{ox} + 55.9$) [11] are found to be reasonably constant, 81.6 (lit., 81.2 [9], 81.7 [13], and 82.9 [14]), 79.4, 79.5, and 79.8 kcal/mol for **1H**, **2H**, **3H** and **4H**, respectively, within experimental error (Table 2).

It is concluded that t-butylcyclopentadienide ions become less stable with an increase in the number of substituent most probably owing to a decrease in solvation and an increase in inductive effect.

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