Remarkably Large Captodative Stabilisation in Radical Ions

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Radical ions are calculated to have large nonadditive captodative stabilisation, in contrast to their neutral analogues.

The synergetic stabilising influence of a combination of an acceptor and a donor substituent at a radical centre, termed the captodative (cd) effect, has been suggested to play a crucial role in a number of reactions proceeding *via* radical and diradical intermediates.[1,2] However, many neutral radicals with prototypical captodative substituents fail to show any extra stabilisation under critical experimental[3] and theoretical scrutiny.[4,5] We now show that cd stabilisation is unambiguously large in radical ions.

The possibility of nonadditive substituent interactions in radical ions, *e.g.* (**1**)—(**4**), has been suggested earlier.[1c,d] However, the cd effect in radical ions has not yet been quantitatively established. We have chosen to quantify the effect in two representative radical anions, (**5**) and (**6**), derived from the neutral captodative radicals, (**7**) and (**8**), respectively, using the same theoretical levels used recently.[5] Experimental[3] and theoretical[4,5] studies on (**7**) and related models have shown that the substituent combination of CN and OH (or OR) fails to lead to any extra stabilisation relative to corresponding monosubstituted radicals. On the other hand, (**8**) represents the neutral radical computed to have the largest synergetic stabilisation so far.[5,6]

Comparison of the radical stabilisation energy (RSE) of a disubstituted methyl radical [energy of the isodesmic reaction (1)] with the sum of the RSEs due to the corresponding monosubstituted radicals [energies of reactions (2), with X = D and A] provides a direct measure of the cd effect, CDE(1).[5,6] The estimate for (**5**) is found to be 11 kcal/mol (cal = 4.184 J) at the ROHF/4-31G level with full geometry optimisation of all species involved,[7] a value nearly as large as that obtained for (**8**) (Table 1).

$$\mathrm{CHDA^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + CH_2DA} \tag{1}$$

$$\mathrm{CH_2X^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + CH_3X} \tag{2}$$

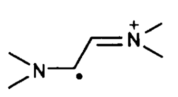
The cd effect is even more spectacular for (**6**). The nonadditivity in RSEs in this system is as large as 43 kcal/mol, more than three times the value in the neutral analogue (**8**). Additional UHF/3-21G calculations indicate an even larger cd effect in (**6**). The extra stabilisation is calculated to be 58 kcal/mol, with a total RSE of nearly 100 kcal/mol. Even allowing for errors resulting from the limitations in the computational methods employed (particularly due to the lack of diffuse functions in the basis set),[8] the calculated energetics compel attention to a dramatic electronic effect.

Table 1. Calculated radical stabilization energies and estimates of the captodative effect (kcal/mol).

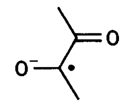
	Species	MNDO	ROHF/ 4-31G	UHF/ 3-21G
RSE:				
	$H_2C^{\cdot}NH^-$	24.2	27.4	30.5
	$H_2C^{\cdot}BH_2$	6.0	11.7	11.3
	$HC^{\cdot}(BH_2)NH^-$	62.0	82.5	99.7
	$H_2C^{\cdot}O^-$	18.2	21.9	27.5
	$H_2C^{\cdot}CN$	3.7	5.3	11.8
	$HC^{\cdot}(CN)O^-$	31.6	38.2	46.6
CDE(1):[a]				
	$HC^{\cdot}(BH_2)NH^-$	31.8	43.4	57.9
	$HC^{\cdot}(BH_2)NH_2$	7.3	12.0	—
	$HC^{\cdot}(CN)O^-$	9.7	11.0	7.3
	$HC^{\cdot}(CN)OH$	0.8	0.2	—
CDE(2):[b]				
	$HC^{\cdot}(BH_2)NH^-$	31.0	45.3	58.6
	$H_2C(BH_2)NH^-$	−0.8	1.9	0.8
	$HC^{\cdot}(BH_2)NH_2$	3.6	12.0	—
	$H_2C(BH_2)NH_2$	−3.7	0.1	—
	$HC^{\cdot}(CN)O^-$	23.7	38.3	35.9
	$H_2C(CN)O^-$	14.0	27.4	28.7
	$HC^{\cdot}(CN)OH$	−2.8	−1.2	—
	$H_2C(CN)OH$	−3.6	−1.4	—

[a] CDE(1) = RSE(AD) − RSE(A) − RSE(D). [b] Energy of reaction (3) for radicals and radical ions; energy of reaction (4) for even electron species.

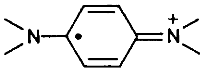
Large nonadditivity in RSEs may also result from destabilising ground state electronic effects in the reference even electron cd system.[3—5] To take this factor into account, the cd effect in the radical and in the parent even electron species have been individually computed using alternative isodesmic reactions (3) and (4), respectively. The calculated energy, CDE(2), for $CH_2(CN)O^-$ (27 kcal/mol: ROHF/4-31G) indicates that the even electron species is in fact stabilised by the σ



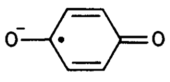
(1)



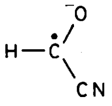
(2)



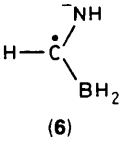
(3)



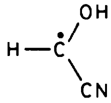
(4)



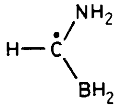
(5)



(6)



(7)

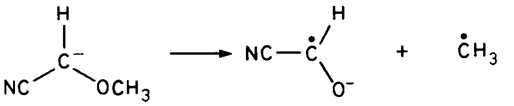


(8)

and polarisation effects of the substituents. Therefore, the alternative estimate, CDE(2), for the cd stabilisation for **(5)** is even larger (38 kcal/mol). However, a similar analysis for NH_2, BH_2, and NH^-, BH_2 pairs indicates no nonadditivity for the even electron systems. Therefore, the total cd effect estimates, CDE(2), for the corresponding radicals are almost identical to the CDE(1) values.

$$CHDA^{\cdot} + CH_3^{\cdot} \rightarrow CH_2D^{\cdot} + CH_2A^{\cdot} \quad (3)$$

$$CH_2DA + CH_4 \rightarrow CH_3D + CH_3A \quad (4)$$



$$NC-\overset{H}{\underset{OCH_3}{C^-}} \longrightarrow NC-\dot{C}(H)-O^- + \dot{C}H_3 \quad (5)$$

Independent evidence for the magnitude of the cd effect was obtained by computing the rotational barriers about the C–B bond in **(6)** and in $CH_2{}^{\cdot}BH_2$. The barrier in the former is larger by 43.2 and 54.8 kcal/mol at the ROHF/4-31G and UHF/3-21G levels, respectively. These values are very close to the CDE(1) estimates at the same theoretical levels confirming that these values correspond to the cd effect resulting from extended π conjugation.

Additional MNDO[9] calculations indicate that the enhanced cd effect in radical ions may be a general phenomenon. Nonadditivity in the substituent effects ranges from 10 to 32 kcal/mol for radical anions with O^- and NH^- as the donor and CN, CHO, and BH_2 as the acceptor and for radical cations with NH_2 as the donor and CNH^+, $CHOH^+$, and $CHNH_2{}^+$ as the acceptor. The alternative CDE(2) estimates are also similar in magnitude for these radical ions, with the exception of radical anions with CN and CHO acceptors for which the CDE(2) values are even larger. Considering the underestimation of the cd effect in **(5)** and **(6)** by the MNDO method, the values for the radical ions are indeed significant.

The enhanced cd stabilization in radical ions relative to neutral radicals is consistent with the PMO explanation for the effect.[1c,6] A donor pushes up the SOMO of the radical enabling the latter to interact more effectively with an acceptor. Equivalently, an acceptor brings down the SOMO leading to a better energy match with a donor. The donor orbitals in O^- and NH^- are higher in energy than the lone pairs of neutral OR and NR_2 groups and so can increase the energy of the SOMO to a greater extent. Similarly, the acceptor orbitals of protonated cyano, formyl, and imino groups can lower the SOMO more effectively than their neutral counterparts. Therefore, the co-operative interaction involving the donor–acceptor pair is greater in the charged systems.

These results have important consequences in gas phase ion chemistry. Many mass spectral fragmentation pathways may well be determined by the large magnitude of cd stabilisation in radical ions. Striking evidence is available from a collisional activation study on the $(M - H)^-$ ion of methoxyacetonitrile. This species showed a surprising preference for a homolytic bond cleavage [reaction (5)],[10] constituting an interesting example of the violation of the 'even electron rule'.[11] The methyl loss was also noteworthy because the product ion concentration was one of the highest ever measured in such a double resonance experiment.[10] These remarkable results may be attributed directly to the cd stabilisation associated with the product, **(5)**.

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