Charge Localization by the Gegenion: the Electronic Structure and Energies of the Alkali Metal Acetaldehyde Enolates

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According to *ab initio* calculations on model alkali metal acetaldehyde enolate monomers $CH_2{=}CH{-}O^-M^+$, the metal gegenion-induced negative charge localization on the enolate oxygen shows little variation along the Li–Cs series and reduces the stabilization of the enolate anion (33 kcal mol^{-1} *vs.* OH^{-1}) to only 9–14 kcal mol^{-1} *vs.* MOH in the metal derivatives (1 cal = 4.184 J).

Alkali metal enolates, widely used synthetic reagents in organic sythesis, are stabilized by π-delocalization.[1] The contribution **1b** to the enolate anion resonance hybrid is significant. However, this stabilizing effect is counteracted by the metal cation. Although the overall cation–anion interaction is highly favourable coulombically, it serves to localize the charge on oxygen in the anion (*i.e.*, **2b** contributes relatively less than **1b**).[2] By means of *ab initio* pseudopotential calculations,[3]† we demonstrate the extent to which ion pair interactions influence the geometries, electronic structures and stabilization energies. The presence of the gegenion has a large effect, but surprisingly, there is little variation among the alkali metal cations despite the great differences in their ionic radii.

Table 1 shows the optimized geometries and the total and π-natural charges for vinyl alcohol, the acetaldehyde enolate anion and the Li–Cs alkali metal acetaldehyde enolates. The unbridged $M{-}O{-}CH{=}CH_2$ minima‡ were chosen for investigation as these model the M–O interactions in the aggregates found in the crystal structures as well as those expected in solutions.[15]

All the metal ions have near unit charges (0.96–1.00); the Li^+ charge is only slightly less than that of the remaining alkali metal cations. Such almost fully ionic M^+X^- bonding involving all the alkali metals is general when strongly electronegative groups are involved.[13] Both the total and the π-charges on oxygen are distinctly less in the free enolate anion than in the metal enolates. The polarizing, charge localizing influence of the cations (*cf.* **2a**) is responsible for the larger oxygen charges in the alkali metal enolates. However, there is only a slight decrease from the Li to the other alkali metal enolates.

The charge on C-2 is of particular interest, since this is the desired site for electrophilic attack. This charge is highest in the free enolate anion (*cf.* **1b**), and lowest in the vinyl alcohol. The C-2 charges in the alkali metal enolates are significantly smaller than in the free anion, but increase only slightly from the Li to the other metal enolates. The contribution of **2b** is smaller due to the gegenion-induced charge localization.

The influence of the gegenion on the geometries also is apparent. The C(1)–C(2) distance is shortest in the vinyl alcohol (1.318 Å) (with its only modest neutral resonance stabilization). The C–C length increases to 1.332 Å in CH_2CHOLi but then only *ca.* 0.01 Å in going along the alkali metal enolate series. The free enolate anion has by far the longest C–C distance (1.372 Å). The variations in the C–O separations are complementary. The shortest distance (1.244 Å) is found in the enolate anion and the largest (1.340 Å) in vinyl alcohol. Owing to the CO double bond character, the values in the metal enolates are intermediate (*ca.* 1.29 Å). Again, CH_2CHOLi is set somewhat apart from the other metal enolates.§

The stabilization of the enolate anion is very large [eqn. (1)].[16] Charge localization due to the gegenion reduces the stabilization energies dramatically (*cf.* eqn. 2), much more than is found generally in R^- *vs.* R^-M^+ compounds (*e.g.* the attenuation factor of 0.73 for M = Li[17]). The metallation energies of vinyl alcohol with the alkali metal hydroxides are still exothermic [eqn. (2)] since the alkali metal enolates are stabilized, *e.g.* by charge delocalization (*cf.* **2**), relative to the localized alkali metal hydroxides.

$$H_2C{=}CHOH + OH^- \rightarrow H_2C{=}CHO^- + H_2O \qquad (1)$$

$-32.5\,\mathrm{kcal\,mol^{-1}}$ [MP2 (full)-pseudopot. calc.]
$(-33.0\,\mathrm{kcal\,mol^{-1}})$ [MP2(full)/6-31+G*//MP2(full)/6-31+G*]
$-33.5\,\mathrm{kcal\,mol^{-1}}$ (exp., ref. 16)

$$H_2C{=}CHOH + MOH \rightarrow H_2C{=}CHOM + H_2O \qquad (2)$$

M	Metallation energy/kcal mol^{-1}
Li	-9.4^a $(-8.2)^b$
Na	-12.3^a $(-11.0)^b$
K	-13.2^a
Rb	-13.7^a
Cs	-12.9^a

[a] MP2(full)-pseudopot. calc. [b] MP2(full)/6-31 + G*//MP2(full)/6-31 +G*.

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† All enolate geometries were optimized in C_s-symmetry at the HF level using the gradient optimization techniques implemented in the GAUSSIAN 90 program.[4] Only the M–O distances for the K, Rb and Cs enolates were reoptimized at MP2 by employing the appropriate fixed HF geometry for each enolate moiety. However, the changes in M–O distances were negligible. The following valence-electron effective-core-potentials (ve-ecp) were used for all optimizations and single point calculations: 4- and 6-ve-ecp replace the [1s] core of carbon and oxygen.[5] 1-ve-ecp were used for Li and Na;[6] 9-ve-ecp for K, Rb, and Cs.[7] Basis set contraction scheme: C, O: (311/311/1),[8-10] Li, Na: (211/31/1);[8,10] K, Rb, Cs: (21111/21111/11)[7,10] H (31).[11] The natural charges refer to HF and the metallation energies to MP2(full) single point calculations using the extended (311/11)[12] hydrogen basis set on the HF optimized geometries for the enolate anion, vinyl alcohol, as well as the Li and Na enolates and on the (partially) MP2 optimized geometries for the K-Cs enolates. The reaction energies are not corrected for zero point vibrational energy since these corrections are very small. For further details concerning the application of the pseudopotential computation on other alkali metal compounds including the alkali metal hydroxides, see ref. 13. For comparison we also carried out all-electron calculations at the MP2(full)/6-31+G*// MP2(full)/6-31+G* level for vinyl alcohol, the enolate anion and the Li and Na enolates.

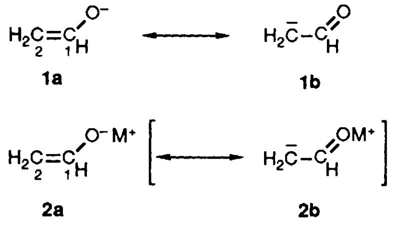
‡ The monomeric bridged Li-enolate structure is 5.1 kcal mol^{-1} [MP2(FU)/6-31G*//MP2(FU)/6-31G*] more stable than the linear structure. For earlier data, see T. J. Lynch, M. Newcomb, D. E. Bergbreiter and M. B. Hall, *J. Org. Chem.*, 1980, **45**, 5005.

§ The known X-ray structures of Li-, Na- and K-enolates do not show any regular variations in the C–C and C–O distances, but different aggregation, solvation and substituents preclude direct comparisons.[15]

Table 1 HF-geometries (Å,°) and natural charges of vinyl alcohol, the alkali metal acetaldehyde enolates and the acetaldehyde enolate anion

M	$d_{C_1C_2}$	d_{C_1O}	d_{OM}	$\angle_{MOC}$	$\angle_{OCC}$	$\rho_{C_2}{}^a$	$\rho_{C_1}{}^a$	$\rho_O{}^a$	$\rho_M{}^a$
H	1.318 (1.339)^b	1.340 (1.370)^b			126.9	−0.498 (−0.176)	0.289 (0.086)	0.749 (−0.913)	
Li	1.332 (1.350)^b	1.296 (1.330)^b	1.613 (1.618)^b	175.2	127.2	−0.571 (−0.272)	0.341 (0.137)	−1.131 (−0.855)	0.962 (0.988)
Na	1.340 (1.356)^b	1.286 (1.322)^b	1.977 (1.978)^b	179.1	128.0	−0.623 (−0.331)	0.365 (0.163)	−1.103 (−0.833)	0.988 (0.998)
K	1.342	1.284	2.289^c (2.293)	171.0	128.1	−0.634 (−0.343)	0.375 (0.168)	−1.101 (−0.826)	0.994 (0.997)
Rb	1.343	1.282	2.447^c (2.449)	170.1	128.2	−0.642 (−0.352)	0.378 (0.172)	−1.093 (−0.820)	0.994 (0.996)
Cs	1.342	1.284	2.547^c (2.554)	170.0	128.1	−0.635 (−0.344)	0.377 (0.169	−1.097 (−0.822)	0.988^d (0.991)^d
—	1.372 (1.386)^b	1.244 (1.284)^b			130.4	−0.790 (−0.513)	0.424 (0.213)	−0.923 (−0.702)	

[a] Natural charges (see ref. 14); π-charges are given in parentheses. [b] MP2(full)/6-31+G*//MP2(full)/6-31+G*-values are given for comparison in parentheses. The C–C and C–O distances are systematically longer than the HF values. However, this does not significantly change the reaction energies for eqns. (1) and (2). [c] The M–O distances are optimized at the MP2 level; the values in parentheses are the HF distances. [d] The small deviations from the monotonous trends are due to small d-orbital occupations.[13]


1a **1b**

2a **2b**

However, no smooth increase in the reaction energies with the increasing O–M distance is found! Even though all the alkali metal enolates are essentially fully ionic, it seems reasonable to expect that the upper limit for the free anion (infinite O–M distance) will be approached as the M–O distance increases. This is not the case. While the reaction energy for Li is smallest (−9.4 kcal mol^{-1}), the increase for the other alkali metals only is modest and the range (*ca.* −12.3 to −13.7 kcal mol^{-1}) is small. The stabilization energy (−33 kcal mol^{-1}) of the free anion is considerably larger.

Owing to charge localization by the gegenions, the resonance stabilization in the alkali metal enolates is reduced by 19 to 24 kcal mol^{-1}! The charge localizing influence is still very effective for long O–M distances (*e.g.* 2.547 Å in CH_2CHOCs) since electrostatic interaction energies decrease for long distances only with r^{-1}. To demonstrate this, we carried out analogous calculations of the reaction energies of eqn. (2) using data for model species in which the alkali metals in both MOH and CH_2CHOM sets are replaced by positive point charges (but using the same fixed geometries). The resulting 'point charge' reaction energies are similar to those given in eqn. (2) above [(MP2(full)-pseudopot. calc.: Li: −5.1; Na: −9.7; K: −11.1; Rb: −12.1; Cs: −11.9 kcal mol^{-1})]. Hence, the reduction in stabilization [eqn. (2) *vs.* eqn. (1)] is caused mainly by electrostatic interactions rather than by metal orbital overlap (except for Li, to a minor extent).

The alkali metal-enolate ion pair interactions influence the geometries, the charge distributions, and the reaction energies similarly. With the modest exception of Li, the alkali metal cations do not display the gradation of behaviour expected due to the increasing ionic radius. Destabilization due to charge localization can be expected to be of general importance in polar organometallic chemistry.

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References

1 M. Schlosser, *Strukturen und Reaktivität polarer Organometalle*, Springer, Berlin, 1973; L. M. Jackman and B. C. Lange, *Tetrahedron*, 1977, **33**, 2737; O. A. Reutov, I. P. Beletskaya and A. L. Kurts, *Ambident Anions*, Consultants bureau, New York, 1983; C. H. Heathcock, in *Modern Synthetic Methods*, ed. R. Scheffold, Verlag Helvetica Chimica Acta and VCH, Basel and Weinheim, 1992, vol. 6, p. 1.

2 C. Schade, P. v. R. Schleyer, M. Geißler and E. Weiss, *Angew. Chem.*, 1986, **98**, 922; C. Schade and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1987, **27**, 169.

3 L. Szasz, *Pseudopotential Theory of Atoms and Molecules*, Wiley, New York, 1985.

4 M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, GAUSSIAN, Inc., Pittsburgh PA, 1990.

5 G. Igel-Mann, H. Stoll and H. Preuss, *Mol. Phys.*, 1984, **80**, 3297.

6 P. Fuentealba, O. Reyes, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **87**, 5338.

7 C. Lambert, M. Kaupp, P. v. R. Schleyer, M. Dolg, A. Bergner and H. Stoll, to be submitted.

8 M.-J. Poppe, G. Igel-Mann, A. Savin and H. Stoll, unpublished results.

9 T. Clark, J. Chandrashekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.

10 S. Huzinaga, *Gaussian basis sets for molecular calculations*, Elsevier, Amsterdam, 1984.

11 T. H. Dunning and H. Hay, in *Methods of Electronic Structure Theory*, ed. H. F. Schaefer III, Plenum Press, Oxford, 1977.

12 P. Botschwina and W. Meyer, *Chem. Phys.*, 1975, **63**, 2356.

13 C. Lambert, M. Kaupp and P. v. R. Schleyer, *Organometallics*, in the press.

14 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

15 D. Seebach, *Angew. Chem.*, 1988, **100**, 1685; P. G. Williard, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 1, p. 1 and literature cited therein.

16 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, Suppl. 1, **17**, 1988; F. Turecek and Z. Havlas, *J. Org. Chem.*, 1986, **51**, 4066.

17 P. v. R. Schleyer, E. Kaufmann, G. W. Spitznagel, R. Janoschek and G. Winkelhofer, *Organometallics*, 1986, **5**, 79.