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Are the Oxocarbon Dianions Really Aromatic?

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Abstract: The graph theory of aromaticity was applied to the oxocarbon conjugated systems. Contrary to the prediction by West et al., dianions of most monocyclic oxocarbons, together with all the neutral ones, were predicted to have very small resonance energies. The deltate dianion alone was predicted to be highly aromatic. This ion alone was predicted to be highly diatropic, too.

Introduction

In 1960, West et al. expressed their view that monocyclic oxocarbon dianions of general formula $C_nO_n^{2-}$ might represent a new class of aromatic substances.[1-5] Here, the term "oxocarbon" designates compounds in which all, or nearly all, of the carbon atoms bear ketonic oxygen functions.[3] The most famous oxocarbons are monocyclic ones. At present, four such species are known, deltate (I), squarate (II), croconate (III), and rhodizonate (IV) dianions.[3,6] According to West et al.,[1,3] evidence supporting the aromaticity was provided by a study of their vibrational spectra, which show that they have symmetric D_{nh} structures.[7,8] The C–C stretching force constants for the oxocarbon dianions are considerably larger than those for the C–C single bonds, indicating π-electron delocalization over the oxocarbon ring. Large delocalization energies were consistent with this observation.[2]

However, Dewar et. al.[9] and Hess and Schaad[10] pointed out that delocalization energy cannot be used as a measure of aromatic stabilization. Almost all conjugated systems, even very labile ones, are known to have significant delocalization energies. Delocalization energies of familiar carbocyclic systems can never be arranged in the experimental order of stability.[11] The present consensus is that any aromaticity index of a cyclic conjugated system must be related to some thermodynamic stability estimated relative to an appropriate olefinic reference structure.[9-15]

We have been developing the graph theory of aromaticity since 1975.[12,13] It has then been established that this theory satisfies this consensus exactly. We could successfully predict aromaticities of a wide variety of cyclic conjugated systems, both neutral and ionic, by means of this theory.[12-15] The tendency toward electrophilic substitution reactions[16] has often been employed as an experimental indication of aromaticity. However, this concept cannot be applied to the oxocarbon conjugated systems. Therefore, I think that our graph theory of aromaticity alone[12-17] will give a reasonable solution to whether or not cyclic oxocarbon dianions have positive resonance energies due to aromaticity. I wish to reexamine the aromaticities of the monocyclic oxocarbons and their dianions along this line. The diamagnetic susceptibilities due to ring currents will also be examined. The Hückel molecular orbital (HMO) model is used throughout this paper.

Table I. Resonance Energies of the Neutral Oxocarbons

species	resonance energy,[a] β $h = 1.0$, $k = 0.8$	$h = 0.2$, $k = 1.6$	$h = 0.22$, $k = 0.99$
C_3O_3	0.197 (0.066)	0.015 (0.005)	0.050 (0.017)
C_4O_4	−0.016 (−0.004)	−0.023 (−0.006)	−0.070 (−0.017)
C_5O_5	−0.035 (−0.007)	−0.001 (−0.000)	−0.009 (−0.002)
C_6O_6	−0.008 (−0.001)	0.001 (0.000)	0.008 (0.001)
C_7O_7	0.003 (0.000)	0.000 (0.000)	0.002 (0.000)
C_8O_8	0.002 (0.000)	−0.000 (−0.000)	−0.001 (−0.000)

[a] Values in parentheses are resonance energies per unit structure.

Table II. Resonance Energies of the Oxocarbon Dianions

species	resonance energy,[a] β $h = 1.0$, $k = 0.8$	$h = 0.2$, $k = 1.6$	$h = 0.22$, $k = 0.99$
$C_3O_3^{2-}$ (I)	0.338 (0.113)	0.159 (0.053)	0.147 (0.049)
$C_4O_4^{2-}$ (II)	0.060 (0.015)	0.057 (0.014)	−0.017 (−0.004)
$C_5O_5^{2-}$ (III)	0.013 (0.003)	0.050 (0.010)	0.025 (0.005)
$C_6O_6^{2-}$ (IV)	0.025 (0.004)	0.037 (0.006)	0.031 (0.005)
$C_7O_7^{2-}$ (V)	0.027 (0.004)	0.026 (0.004)	0.019 (0.003)
$C_8O_8^{2-}$ (VI)	0.021 (0.003)	0.020 (0.002)	0.012 (0.001)

[a] Values in parentheses are resonance energies per unit structure.

Resonance Energies of the Oxocarbon Conjugated Systems

Resonance energies of the six oxocarbon conjugated systems I–VI were calculated according to our graph theory of aromaticity.[18] They are listed in Tables I and II. Three sets of parameters were used to describe carbonyl groups in these compounds: one determined by West and Powell ($h = 1.0$ and $k = 0.8$),[2] one by Baenziger and Hegenbarth ($h = 0.2$ and $k = 1.6$),[19] and one by Hess, Schaad, and Holyoke ($h = 0.22$ and $k = 0.99$).[20]

First, the resonance energies based on the parameters of Hess et al.[20] are best suited for the aromaticity consideration of the neutral oxocarbons C_nO_n, because these parameters were deter-

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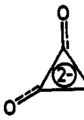
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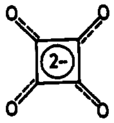
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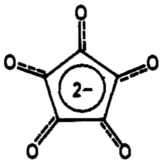
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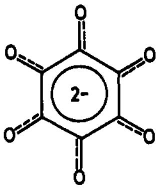
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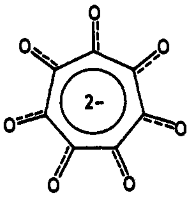
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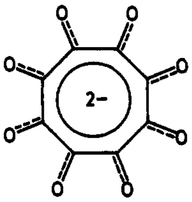

VI

mined so as to reproduce heats of atomization of neutral carbonyl compounds.[20] As is readily seen from Table I, neutral oxocarbons are all predicted to be substantially nonaromatic with negligible resonance energies. For reference, resonance energies of familiar carbocyclic systems are as follows: benzene, 0.273β; fulvene, 0.020β; *o*-xylylene, 0.059β; *p*-xylylene, 0.061β; dimethylenecyclobutene, −0.163β; cyclooctatetraene, −0.595β; [10]annulene, 0.159β.[12,13] Among these compounds, *o*- and *p*-xylylenes and fulvene are considered to be olefinic in nature. All neutral oxocarbons with similar resonance energies can assuredly be regarded as nonaromatic species.

For normalization of the resonance energy RE with respect to the size of the conjugated system, a new quantity is defined as RE/n for $C_nO_n^{m-}$, where $m = 0$ or 2. This is termed the resonance energy per unit structure (REPUS). For all neutral oxocarbons, REPUS is smaller than 0.017β. Such olefinic character of the compounds resembles that of radialenes.[12,13,21] As both systems exist in only one canonical structure, it may be improbable that they are either markedly aromatic or markedly antiaromatic. As in the case of [4]radialene, C_4O_4 is predicted to be slightly antiaromatic.

The above prediction is quite consistent with the fact that these compounds cannot retain their cyclic conjugated systems in the presence of water.[3,22] Oxidation of squaric, croconic, or rhodizonic acid leads to the fully hydroxylated structure of the general formula $C_n(OH)_{2n}$. These perhydroxycycloalkanes are again reactive and show no strong infrared absorption in the carbonyl region. The most distinct feature of aromatic compounds is the retention of the original cyclic conjugated system even if they are exposed to somewhat disturbing conditions.[23] The neutral oxocarbons are undoubtedly olefinic from this viewpoint.

Next, the resonance energies based on the parameters of Baenziger and Hegenbarth[19] appear to be better suited for the oxocarbon dianions, because these parameters were chosen so as to best reproduce the bond orders in the oxocarbon dianion of medium size, i.e., $C_5O_5^{2-}$. In fact, Patton and West also applied a similar set of parameters ($h = 0.3$ and $k = 1.4$) to anion radicals of the monocyclic oxocarbons.[24] Contrary to the prediction by West et al.,[1-5] all oxocarbon dianions but the deltate are then predicted to be substantially nonaromatic with negligibly small resonance energies (Table II). For II–VI, REPUS is smaller than 0.015β. By reference to REPUS of the neutral oxocarbons, this can be interpreted as an indication of the absence of aromaticity. The deltate dianion alone shows exceptionally large resonance energy, more than half that of benzene.

The oxocarbon dianions are apparently stable both in aqueous solution and in the solid state.[3,6,25] However, the stability of II–IV might be ascribed to the kinetic stability rather than to the thermodynamic one. The rhodizonate dianion is very unstable in basic media; it is readily rearranged to form a croconate dianion.[3] This indicates that it is not easy to retain its original cyclic conjugated system in such a mild condition. The other known oxocarbon dianions do not undergo any molecular rearrangement, but the condensation products can be easily obtained on treatment of II–IV with malononitrile.[26] The unknown dianions $C_7O_7^{2-}$ and $C_8O_8^{2-}$ can likewise be predicted to be nonaromatic.

Table III. Diamagnetic Susceptibilities of the Neutral Oxocarbons Due to Ring Currents

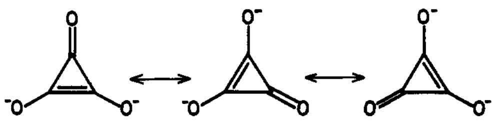
species	diamagnetic susceptibility $h = 1.0$, $k = 0.8$	 $h = 0.2$, $k = 1.6$	 $h = 0.22$, $k = 0.99$
C_3O_3	$0.190\Theta_3{}^2\beta$	$0.016\Theta_3{}^2\beta$	$0.057\Theta_3{}^2\beta$
C_4O_4	$-0.014\Theta_4{}^2\beta$	$-0.023\Theta_4{}^2\beta$	$-0.071\Theta_4{}^2\beta$
C_5O_5	$-0.035\Theta_5{}^2\beta$	$-0.001\Theta_5{}^2\beta$	$-0.008\Theta_5{}^2\beta$
C_6O_6	$-0.008\Theta_6{}^2\beta$	$0.001\Theta_6{}^2\beta$	$0.008\Theta_6{}^2\beta$
C_7O_7	$0.003\Theta_7{}^2\beta$	$0.000\Theta_7{}^2\beta$	$0.002\Theta_7{}^2\beta$
C_8O_8	$0.002\Theta_8{}^2\beta$	$-0.000\Theta_8{}^2\beta$	$-0.001\Theta_8{}^2\beta$

Table IV. Diamagnetic Susceptibilities of the Oxocarbon Dianions Due to Ring Currents

species	diamagnetic susceptibility $h = 1.0$, $k = 0.8$	 $h = 0.2$, $k = 1.6$	 $h = 0.22$, $k = 0.99$
$C_3O_3^{2-}$ (I)	$0.294\Theta_3{}^2\beta$	$0.129\Theta_3{}^2\beta$	$0.131\Theta_3{}^2\beta$
$C_4O_4^{2-}$ (II)	$0.045\Theta_4{}^2\beta$	$0.040\Theta_4{}^2\beta$	$0.030\Theta_4{}^2\beta$
$C_5O_5^{2-}$ (III)	$0.003\Theta_5{}^2\beta$	$0.039\Theta_5{}^2\beta$	$0.018\Theta_5{}^2\beta$
$C_6O_6^{2-}$ (IV)	$0.018\Theta_6{}^2\beta$	$0.030\Theta_6{}^2\beta$	$0.027\Theta_6{}^2\beta$
$C_7O_7^{2-}$ (V)	$0.022\Theta_7{}^2\beta$	$0.021\Theta_7{}^2\beta$	$0.015\Theta_7{}^2\beta$
$C_8O_8^{2-}$ (VI)	$0.017\Theta_8{}^2\beta$	$0.016\Theta_8{}^2\beta$	$0.009\Theta_8{}^2\beta$

On the other hand, the deltate dianion has a much larger REPUS (0.053β). We might safely say that this is a typical aromatic substance, although there is no direct experimental evidence for the presence of aromaticity. We have tacitly assumed that the increased strain and charge density in the deltate ion are retained in the olefinic reference structure and that aromaticity is primarily due to the π electrons. Then, it is true that the deltate dianion has a very large vertical resonance energy, on the condition that the cations are loosely bound to it. This inference does not depend upon the choice of parameters (see Table II). The pK_2 values of oxocarbon acids increase as the ring size decreases, going from cróconic to deltic acid.[4] As pointed out by West,[4] this possibly reflects increased charge repulsion in the smaller rings. The apparent stability of the deltate ion may thus be a bit smaller than expected from the resonance energy.

The observed trend in the ^{13}C chemical shifts of the dianions indicates that the C–O bonds become progressively polarized on going from rhodizonate to squarate.[22] This experimental result can be reproduced by the HMO calculations and suggests that the cyclopropenone-like structures such as Ia–c are important in


Ia Ib Ic

describing the conjugated system of the deltate ion. Note that cyclopropenone has been classified as aromatic.[12,13,20,27,28] Its high degree of stability, relative to that of cyclopropanone, is indeed suggestive of its aromatic character.[20,29]

For most oxocarbons, both neutral and ionic, the resonance energies based on the three sets of parameters are comparable to each other. However, the parameters of West and Powell[2]

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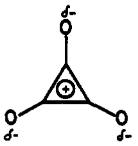
enhance the aromaticity of C_3O_3 alone to a considerable extent. This is probably due to the accidental formation of a cyclic 2-π-electron system along the three-membered ring. In this case, the compound might be regarded as a trisubstituted cyclopropenium ion (Id). This implies that, if the parameters of West and Powell would really represent carbonyl groups of the neutral oxocarbons as well, C_3O_3 could be considered to be aromatic, as in the case of its dianion.



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Diamagnetic Susceptibilities of the Oxocarbon Conjugated Systems

If any of the oxocarbon dianions were aromatic at all, it should be expected to sustain a diamagnetic ring current.[5,17] For this to be seen, diamagnetic susceptibilities of the oxocarbon conjugated systems due to ring currents were calculated by means of our graph theoretical method.[17] The results are presented in Tables III and IV. In these tables

$$\Theta_n = \frac{eS_n}{\hbar c} \tag{1}$$

where S_n is the area of the n-membered carbon ring and the other symbols have their usual meaning.

Recently, Haddon[30] and I[31] proved that, for aromatic annulenes, the susceptibility of a conjugated system, χ_π, is related to the resonance energy, RE, in this manner

$$\mathrm{RE} \propto \frac{\chi_\pi}{\Theta_n^2} \tag{2}$$

This indicates that the susceptibility normalized with respect to the area of the ring squared rather than the susceptibility itself is a good measure of the aromaticity for aromatic annulenes. It seems quite likely that such reasoning is applicable to the other types of monocyclic conjugated systems. If we set all the $\Theta_n^2\beta$ values in Tables III and IV equal to some constant, the figures obtained will give the normalized susceptibilities of the oxocarbon conjugated systems. By surveying Tables I–IV, we can readily notice not only that the sign of the susceptibility exactly agrees with that of the corresponding resonance energy but also that the magnitude of the normalized susceptibility varies in parallel with that of the resonance energy. Therefore, even if we adopt the traditional magnetic criterion of aromaticity,[5,17] we can reach the same conclusion that $C_3O_3^{2-}$ alone is predicted to be highly aromatic. This ion has much larger normalized susceptibility than any other oxocarbon species,[32] so it must be highly diatropic.

Concluding Remarks

It has been widely accepted that the planarity of a conjugated system is not always considered to be of aromatic origin.[35] The example is tropone. Furthermore, the presence of negative resonance energy does not always imply that disruption of cyclic conjugation would lead to stabilization of the antiaromatic system. This point is well illustrated by 1,5-didehydro[12]annulene,[36] which is flexible enough to assume a conformation where cyclic conjugation can be actually disrupted. This antiaromatic compound is still stabilized through cyclic conjugation. Therefore, the planarity and cyclic conjugation of the oxocarbon dianions cannot be viewed as significant evidence for the existence of aromaticity. This study shows that an appreciable degree of aromaticity cannot be expected in II–VI. Decisive experimental evidence will be needed if one wants to insist on the existence of aromaticity in these dianions.

Acknowledgment. This work was supported by the Nishina Memorial Foundation. All the calculations were carried out at the Hokkaido University Computing Center. Suggestions and comments by Professor R. West are gratefully acknowledged.

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(32) In this connection, West et al. analyzed a diamagnetic anisotropy of diammonium croconate[5] and estimated the anisotropy of the croconate ion to be -15×10^{-6} cgs units.[33] This ring current anisotropy appears to be about half that of benzene (-33×10^{-6} cgs units).[34] However, as suggested by West,[5] an available list of local atom and group anisotropies[34] may be unsuitable for the ionic conjugated systems containing heteroatoms. The present study shows that the diamagnetic susceptibility of the croconate conjugated system is less than one-twelfth that of the benzene conjugated system ($0.222\ \Theta_6^2\beta$).

(33) A conversion factor to the SI system is $4\pi \times 10^{-6}$ m^3/cm^3.

(34) Benson, R. C.; Norris, C. L.; Flygare, W. H.; Beak, P. *J. Am. Chem. Soc.* **1971**, *93*, 5591. Norris, C. L.; Benson, R. C.; Beak, P.; Flygare, W. H. *Ibid.* **1973**, *95*, 2766.

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