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THE SPECIFICITY OF THE OZONIZATION OF POLYCYCLIC AROMATICS

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THE reaction of ozone with polycyclic aromatics has received much attention in recent years.[1-6] Moriconi *et al.*,[1-4] Copeland *et al.*[5] and Bailey *et al.*[6] thus have studied the ozonolysis of naphthalene,[6] anthracene,[5,6] naphthacene,[3,5] phenanthrene,[1,5,6] chrysene,[5] benz(a)-anthracene,[2,5] dibenz(a,h)anthracene,[4] triphenylene,[5] perylene,[5] pyrene,[6] and acenaphthylene.[5] Ozone was found to react in most cases by 1,2-addition to aromatic bonds to give ultimately aldehydes and acids presumably via Criegee's[7] Zwitterion. In several instances however ozone also reacted by 1,4-addition to para-positions[2,6] possibly via Bailey's[6] mechanism. The major products isolated can be accounted for by postulating a 1,2- or a simultaneous 1,2- and 1,4-addition of ozone to polycyclic

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[2] E. J. Moriconi, W. F. O'Connor and F. T. Wallenberger, *Chem. & Ind.* 22 (1959); *J. Amer. Chem. Soc.* In press.

[3] E. J. Moriconi, W. F. O'Connor and L. Taranko, *Arch. Biochem. Biophys.* In press. (Private Communication).

[4] E. J. Moriconi, G. W. Cogswell, W. J. Schmitt and W. F. O'Connor, *Chem. & Ind.* 1591 (1958).

[5] P. G. Copeland, R. E. Dean and D. McNeil, *Chem. & Ind.* 329 (1959).

[6] P. S. Bailey, *Chem. Rev.* **58**, 965 (1958).

[7] R. Criegee and G. Lohaus, *Ann.* **583**, 6 (1953).

aromatics.[2] Formation of polymeric by-products, presumably derived from partial destructive ozonization quite frequently precludes complete or quantitative assessment of all reaction products.[2,5,6]

Recently a theoretical correlation has been suggested[2] which offered for the first time a consistent explanation why ozone reacts by 1,2-addition with some aromatics and by 1,4-addition with others. Assuming that the preferred course of the reaction depends predominantly upon the relative stability of various ortho and para dihydro structures characteristic of transitional or intermediate ozone adducts, it has been shown that quinone-hydroquinone redox potentials[8] can be used as measure of such stabilities[9] in the correlation with the preferred course of ozonolysis. Unfortunately only few redox potentials have been determined experimentally.

A new and more universally applicable relationship has now been established in form of calculated resonance energy decreases which accompany the reaction. Such resonance energies are available in the literature for ortho positions[10] and were calculated for para positions from para localization energies[11] according to a suggestion of Wheland.[12] A correlation of resonance energies (R.E.) and redox potentials (E_0) with the preferred course of ozonization (Table 1) shows that ozone indeed reacts preferentially with positions which lead to the more stable transitional or

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[8] L. F. Fieser in H. Gilman's Organic Chemistry Vol I (2nd Ed.), p. 159. John Wiley, New York (1945).

[9] G. E. K. Branch and M. Calvin, The Theory of Organic Chemistry p. 303. Prentice Hall, New York (1944).

[10] R. D. Brown, J. Chem. Soc. 3249 (1950).

[11] R. D. Brown, J. Chem. Soc. 691 (1950); 1612 (1951).

[12] G. W. Wheland, Resonance in Organic Chemistry pp. 379-381. John Wiley, New York (1955).

TABLE 1. Preferred 1,2- and 1,4- addition of ozone

Hydrocarbon in C. A. nomenclature	Positions in C. A. numbering	Resonance energy (kcal)	Redox[2,8] potential (V)	Preferred ozonization (Positions)	Reference
Naphthalene	1,2-	20.0	0.501	1,2-	6
	1,4-	27.6	0.534		
Anthracene	1,2-	20.0	0.415	9,10 1,2-	5,6
	1,4-	25.6	0.451		
	9,10-	15.6	0.254		
Naphthacene	1,2-	19.5	—	5,12-	3,5
	1,4-	24.6	—		
	5,12-	13.6	-0.315		
Phenanthrene	1,2-	23.9	0.586	9,10-	1,5,6
	3,4-	24.4	0.571		
	1,4-	29.6	0.598		
	9,10-	16.0	0.410		
Chrysene	1,2-	23.6	—	5,6-	5
	3,4-	23.3	—		
	5,6-	18.1	0.440		
	1,4-	28.6	—		
Benz(a)anthracene	5,6-	15.3	0.380	7,12--5,6	2,5
	7,12-	19.6	0.353		
Dibenz(a, h)anthracene	5,6-	15.7	—	5,6-	4
	7,14-	22.6	0.418		
Triphenylene	1,2-	25.8	—	1,2-	5
	2,3-	32.1	—		
	1,4-	30.0	—		
Pyrene	4,5-	16.0	0.420	4,5	6

intermediate 1,2- or 1,4-adduct, since the lower the R.E.[10] and the E_o,[9] the more stable the corresponding ortho or para dihydro structure.

Most compounds listed in Table 1 except anthracene, benz(a)anthracene and naphthacene react predominantly by 1,2-additions. This is in agreement with theoretical predictions: $R.E._{ortho} < R.E._{para}$ and $E_{o_{ortho}} < E_{o_{para}}$.

Naphthacene[3,5] and anthracene[5,6] give predominantly the corresponding quinones via 1,4-addition of ozone. This likewise is in agreement with the proposed correlations: $R.E._{ortho} > R.E._{para}$ and $E_{o_{ortho}} > E_{o_{para}}$. Small amounts of 2,3-naphthalenedicarboxylic acid were obtained recently from the ozonization of anthracene in addition to large amounts of anthraquinone.[5] The competing 1,2-addition of ozone to the 1,2- and 3,4-bonds of anthracene is accordingly much slower (less preferred) than the 1,4-addition.

Benz(a)anthracene is also capable of both types of reaction. Ozonolysis under different conditions[2,5] gave by 1,4-addition the isolable intermediate benz(a)anthraquinone[2,5] and its further ozonization product 1,2-anthraquinonedicarboxylic acid[2] and by 1,2-addition,4,5-benzdiphenic acid.[5] Redox potentials tend to favor a predominantly 1,4-addition while resonance energies are in favor of a predominantly 1,2-addition. This singular exception among paralleling R. E. and E_o values in Table 1 might well imply that both reaction paths are nearly equivalent. This then is in agreement with the experimental results.

Thus resonance energies have been found to be a powerful tool to account for and to predict the most reactive sites (bonds or positions) of polycyclic aromatics towards ozone. Predictions can be extended[10,11,12] to compounds not listed in this communication. Furthermore, the discussed correlation lends itself to establish an approximate order of decreasing ease of ozonolysis in the series of unsubstituted polycyclic aromatic hydrocarbons with triphenylene as least and naphthacene as most reactive.