AN ACCOUNT OF THE SELECTIVITY IN THE REACTIONS OF NITRILE OXIDES WITH SUBSTITUTED P-BENZOQUINONES BY FMO THEORY.

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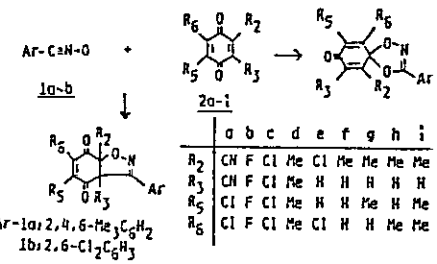
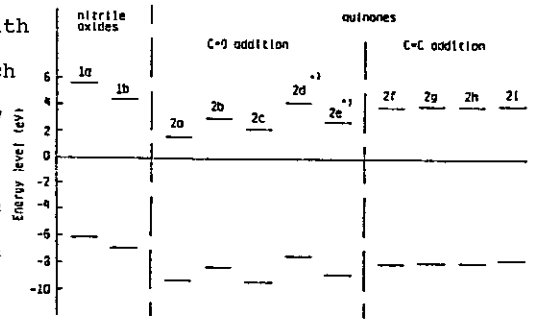
p-Benzoquinones have two kinds of potentially reactive sites, C=C and C=O, and have been known to give two different types of the adducts in the 1,3-dipolar cycloaddition with nitrile oxides. We report here the accounts of the selectivity of the reactions by applying FMO theory. The calculation were carried out by ab initio SCF method with STO-3G basis set.[1] The quinones 2a-e, which undergo C=O addition with 1a, have very low LUMO level except for 2e. The energy differences between HOMO of 1a and LUMO of the quinones is much smaller than those between the opposite interaction, suggesting that HOMO(nitrile oxide)-LUMO(quinone) interaction chiefly governs the C=O addition. The kinetic data shown in Table strongly support this suggestion.



	a	b	c	d	e	f	g	h	i
R_2	CN	F	Cl	Me	Cl	Me	Me	Me	Me
R_3	CN	F	Cl	Me	H	H	H	H	H
R_5	Cl	F	Cl	Me	H	H	Me	H	Me
R_6	Cl	F	Cl	Me	Cl	H	H	Me	Me



Energy levels of HOMO and LUMO

*) The reaction with 1a gave C=O adduct, while that with 1b gave C=C adduct.

Rate constants for the reactions

quinone	with 1a	with 1b	mode
	K [l/mol·s]		
2a	3.52	5.98×10^{-2}	C=O
2b	5.18×10^{-2}	1.15×10^{-3}	C=O
2c	1.59×10^{-2}	7.09×10^{-4}	C=O
2g	9.30×10^{-4}	4.94×10^{-3}	C=C
2h	1.50×10^{-3}	5.26×10^{-3}	C=C
2i	4.35×10^{-4}	2.60×10^{-3}	C=C

While in the cases of quinones 2f-i, which undergo C=C addition with 1a, the FMO levels are higher and the energy differences between the two interactions are smaller than those in the cases mentioned above. The participation of LUMO(nitrile oxide)-HOMO(quinone) interaction should be undeniable. The kinetic data support this consideration, i.e. smaller energy difference in the interaction results in higher reaction rate in the C=C addition. This energetical analysis suggested a different reaction pattern of 1b in the reactions with quinones and it was the case that 1b underwent C=C addition with 2d and 2e. Regio-selectivity as well as site-selectivity will also be discussed.

1) N. Kosugi and H. Kuroda, Chem. Phys. Letters 74 (1980) 490; N. Kosugi, Program GSCF2, Program Library, The Computer Center, The University of Tokyo (1981).