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NOTE

Diethyl Azodicarboxylate 에 의한 유기화합물의 수소이탈 반응기구

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Mechanism of Dehydrogenation of Some Organic Compounds by Diethyl Azodicarboxylate

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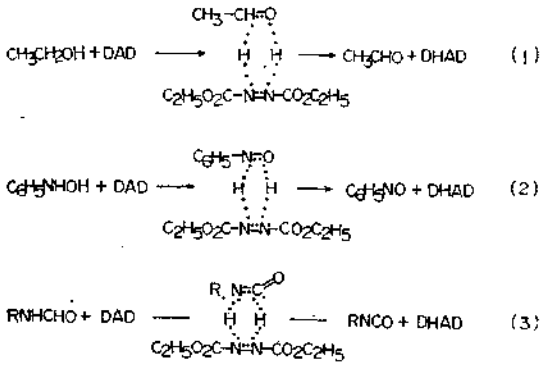
Diethyl azodicarboxylate (DAD) was reported to effect photochemical dehydrogenation of isopropyl alcohol and cyclohexanol,[1,2] and to effect nonphotochemical oxidation of many organic compounds for the last decade. It reacts smoothly with a variety of primary or secondary alcohols, mercaptans, anilines, and hydrazobenzenes to form aldehydes or ketones, disulfides, and azobenzenes. And also it takes place hydrogenation to form diethyl hydrazodicarboxylate (DHAD).[3,4] DAD reacts also with hydroxyamines to give nitroso compounds[5] and with several *N*-monosubstituted formamides to give corresponding isocynates(isolated as urethanes).[6] It is interesting to try to reveal the thermal mechanism of this reaction.

At first glance, the mechanism might be suggested "concerted," since the mechanism of the similar reaction, Diels-Alder reaction, is concerted. For instance, ethanol, phenyl hydroxylamine, and *N*-substituted formamide are used below to illustrate the tentative concerted mechanism:



Based on the molecular orbital approach to chemical reactivity postulated by Fukui,[7~11] Mulliken,[12,13] and Brown,[14] etc., three requirements should be satisfied in order to confirm a concerted mechanism, namely: (1) significant large coefficients of the involved atoms in highest occupied molecular (HOMO) and/or lowest unoccupied molecular orbital (LUMO), (2) same symmetry of the involved atoms in HOMO and/or LUMO, and (3) close energy of the HOMO-LUMO pair. The first requirement must be sa-

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tisfied not only to a concerted mechanism, but also to all the other mechaisms. If the coefficient of an atom in a specified molecular orbital is zero or extremely small, it means that this atom has no contribution to the molecular orbital at all. According to the "frontier electron theory" proposed by Fukui, *et al.*[7,8] this atom could not be involved in the first step of any kinds of reactions. Consequently, we examined the tentative mechanism (1), (2), and (3) from this point of view.

The molecular orbital calculation of diethyl azodicarboxylate was done by simple Hückel Molecular Orbital Theory (HT) by Zweig, *et al.*[15] The required information was given by this author. Calculation of ethanol and phenyl hydroxyamine was done by Extended Hückel Theory (EHT) approach. Bond parameters were used in our choice of dimensions and geometry.[16] For easier computation, methyl, ethyl, and isopropyl formamides were used by CNDO method. The useful parts of the HT, EHT, and CNDO results are shown in *Table* 1, 2, and 3.

The coefficients of the dehydrogenated hydrogens were examined first. It is found from *Table* 2 that one hydrogen in an ethanol molecule has significantly large coefficient while another possesses extremely small one, both in HOMO and LUMO. However, both values are required to be significantly large in order to meet the tentative concerted mechanism (1). As to phenyl hydroxyamine and *N*-substituted formamides, the coefficients of all the concerned hydrogens in HOMO and LUMO are found zero from *Table* 2 and 3. Based on this result and "frontier electron theory," it should rule out not only the tentative concerted mechanism (2) and (3), but also all the other mechanisms which involve those concerned hydrogens.

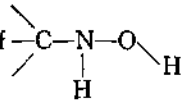
The lowest energy conformations were used for the MO calculation.[17] Several phenyl hydroxyamine conformations were chosen and computed in order to determine the lowest energy one. It was found that the conformation with the skeleton of  planar is the

Table 1. Coefficients of HOMO and LUMO of the nitrogens in diethyl azodicarboxylate, determined by HT method.

Compound	Concerned atoms	HOMO	LUMO
$C_2H_5O_2CN=$ (1)	N(1)[a]	.378	−.526
$NCO_2C_2H_5$ (2)	N(2)[a]	.378	.526

a. the numbers were used to indicate the concerned atoms of the compound on the first column. Same indication was also used in *Table* 2 and 3.

Table 2. Coefficients of HOMO and LUMO of the concerned atoms in ethanol and phenyl hy droxy amine, determined by EHT method.

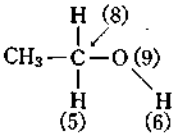
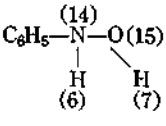
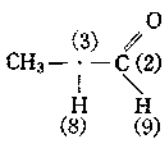
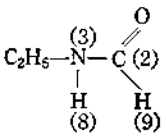
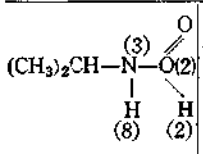
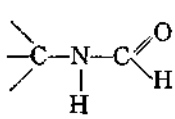
Compounds	Concerned atoms	HOMO		LUMO
	H (5)	S	−.1143	.0382
	H (6)	S	.0413	−.6957
	C (8)	S	.0519	.1465
		P_x	−.4275	.4001
		$_y$	.0849	.7940
			.0479	.0888
	O (9)	S	−.0248	−.0758
		P_x	.5464	.4263
		P_y	−.1689	.5678
		P_z	−.2089	.3801
	H (6)	S	.0000	.0000
	H (7)	S	.0000	.0000
	N (14)	S	.0000	.0000
		P_x	.0000	.0000
		P_y	.0000	.0000
		P_z	−.7020	.0238
	O (15)	S	.0000	.0000
		P_x	.0000	.0000
		P_y	.0000	.0000
		P_z	.3476	−.0170

Table 3. Coefficients of HOMO and LUMO of the concerned atoms in methyl, ethyl, and isopropyl formamides, determined by CNDO method.

Compounds	Concerned atoms	HOMO		LUMO
	H (8)	S	.0000	.0000
	H (9)	S	.0000	.0000
	C (2)	S	−.0000	.0000
		P_x	.0000	.0000
		P_y	−.0000	.0000
		P_z	.1498	−.7669
	N (3)	S	−.0000	−.0000
		P_x	.0000	.0000
		P_y	.0000	.0000
		P_z	−6959	.2904
	H (8)	S	.0000	−.0000
	H (9)	S	.0000	.0000
	C (2)	S	.0000	−.0000
		P_x	−.0000	−.0000
		P_y	−.0000	−.0000
		P_z	−.1442	.7633
	N (3)	S	−.0000	.0000
		P_x	.0000	.0000
		P_y	.0000	.0000
		P_z	.6899	−.2869
	H (8)	S	−.0183	−.0324
	H (9)	S	−.0300	.0030
	C (2)	S	.0025	−.0064
		P_x	−.0001	−.0035
		P_y	.0188	−.0047
		P_z	.1326	.7639
	O (3)	S	.0110	.0307
		P_x	−.0166	.0075
		P_y	−.0225	.0098
		P_z	−.6766	−.2958

most stable (lowest energy) one. The most stable conformation of *N*-substituted formamides was the skeleton of  planar, calculated by EHT and CNDO/2 methods by Hoffman, *et al.*[18]

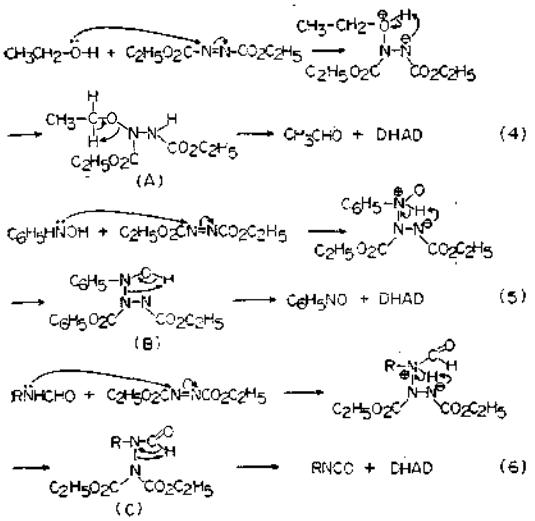
As it is well known, no matter which MO calculation method (such as HT, EHT, CNDO, IMDO, etc.) is used to compute the compounds concerned in this paper, the HOMO and LUMO are contributed only by conjugated π-electron system (composed from p orbitals). Thus, if a hydrogen atom is in the plane of this conjugated system, the contribution of the hydrogen atom to the positive sign lobe of the conjugated p orbitals is equal to the negative sign lobe. The net contributions are then cancelled out each other, and the coefficients of this hydrogen in HOMO and LUMO should be zero. This theoretical consideration is consistent with the result of our calculation. If the planar skeleton of a secondary formamide is distorted, such as rotation of the N—C bond of the formyl group, one hydrogen will gain a very small coefficient value in HOMO and/or LUMO, but another hydrogen is still zero. Therefore, it is neither possible to go through a concerted mechanism. Consequently, the tentative concerted mechanism (1), (2), and (3) are completely ruled out.

A free radical mechanism was then taken into consideration. No obvious information of MO calculation could be obtained to propose a free radical mechanism at this stage of our work. However, based upon our experimental results obtained, we successfully applied thermal dehydrogenation of DAD into the corresponding isocyanates. When the initiator, 2, 2′-azobis-2-methylpropiontrile was separately added to the mixture of *N*-phenyl formamide with DAD and of *N*-cyclohexylformamide with DAD, the reaction rate was not increased at all. As the results of these experiments, a free radical mechanism is not likely.

The ionic mechanism was then considered. The "overlap and orientation" principle proposed by Mulliken[12] has been considered only the

overlap interaction between the HOMO of the donor and the LUMO of the acceptor since it oxidizes a solution of sodium iodide in glacial acetic acid to form iodine quantitatively,[4,19,20] and reacted with alkali metal to give a dianion.[15] The HT clculation indicates that DAD is unusual in possessing a vacant bonding orbital(LUMO).[15] From these facts, it would be expected that DAD might have a high tendency to abstract electron(s) while ethanol, phenyl hydroxyamine, or *N*-secondary formamides etc. should be an electron(s) donor. In this view, the LUMO of DAD and the HOMO of the others were chosen. According to the "frontier electron theory," the element of DAD which has the largest coefficient (absolute value) in LUMO, and the element of the other compounds which has the largest coefficient (absolute) in HOMO should be taken into consideration. Both nitrogens of DAD have the largest value (.526) in LUMO. (The coefficients of other elements of DAD are not shown in *Table* 1 due to the limit of space. Same reason is applied to other compounds in *Table* 2 and 3.

From *Table* 2 and 3, it is found that in HOMO, the oxygen of ethanol, the nitrogen of phenyl hydroxyamine, and the nitrogen of methyl, ethyl, and isopropyl formamides have the largest coefficient with the value |.5464|, |.7020|, |.6959|, |.6899|, and |.6766|, respectively. Accordingly, the ionic mechanism is seem to be plausible and is illustrated as follows:



Aromatic and aliphatic amines, which are electron donor, reacted with DAD to give adducts[21~26] similar to the intermediate of (B) in mechanism (5) and of (C) in (6). By comparison with these experimental results, it is reasonable to propose the intermediates of (B) and (C) (in) the ionic mechanism. The intermediate of (C) is an isoesters of carbamate. It is well known that the products of thermal decomposition of monosubstituted carbamates are isocyanates and alcohols.[27] Therefore, the production of isocynate and DHAD obtaining from the intermediate (C) in mechanism (6) is also very logical.

Conclusion

1. The mechanism of thermal dehydrogenation of organic compounds by diethyl azodicarboxylate seems not likely to be a concerted one, which is proved by the molecular orbital approach.

2. It is neither a free radical mechanism based on the experimental results.

3. Instead, an ionic mechanism is plausible. It could be fully explained by molecular orbital theory. The proposed intermediate (an adduct) could be assumed logically by comparison with some reported reactions,[28] and also the intermediate could be accounted for the formation of the product.

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