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New Kinetic Evidence for Inversional Mechanism in Thermal Geometrical Isomerization about Carbon-Nitrogen Double Bond[†]

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Kinetic pressure and solvent effects were studied for geometrical isomerization about carbon-nitrogen double bond in N,N-dimethyl-N'-[(4-nitrophenyl)methylene]-1,4-benzenediamine and 4-[[4-(dimethylamino)phenyl]imino]-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one. In both of the compounds, the effects clearly demonstrate that the polarity of the reactant decreases slightly during activation, and the results can hardly be reconciled with the previously proposed rotational mechanism.

Thermal Z-E isomerization of azobenzenes generally proceeds via inversional mechanism.[1) The half-lives of Z-isomers may be several hours in many cases. However, the same isomerization proceeds quite rapidly in 4-(dimethylamino)-4'-nitroazobenzene, and it was shown that there are two competitive reaction routes, i.e., inversional and rotational pathways.[2,3) The experimental evidence for this mechanism includes i) large acceleration of the reaction by the increase in the solvent polarity, ii) solvent and temperature dependences of the activation volume, and iii) nonlinear Arrhenius plots in relatively nonpolar solvents.

It has been known for many years that similar thermal isomerization takes place rather rapidly about carbon-nitrogen double bond in various compounds. For example, the half-lives of monosubstituted (Z)-benzylideneanilines are in millisecond region.[4,5) Considering the structural similarities between azobenzene and benzylideneaniline, it is not unreasonable to expect the same inversion-rotation competitive scheme for the latter when it is push-pull substituted as shown in Scheme 1. Furthermore, substituent effect studies in several systems strongly suggest the existence of the two reaction mechanisms in the geometrical

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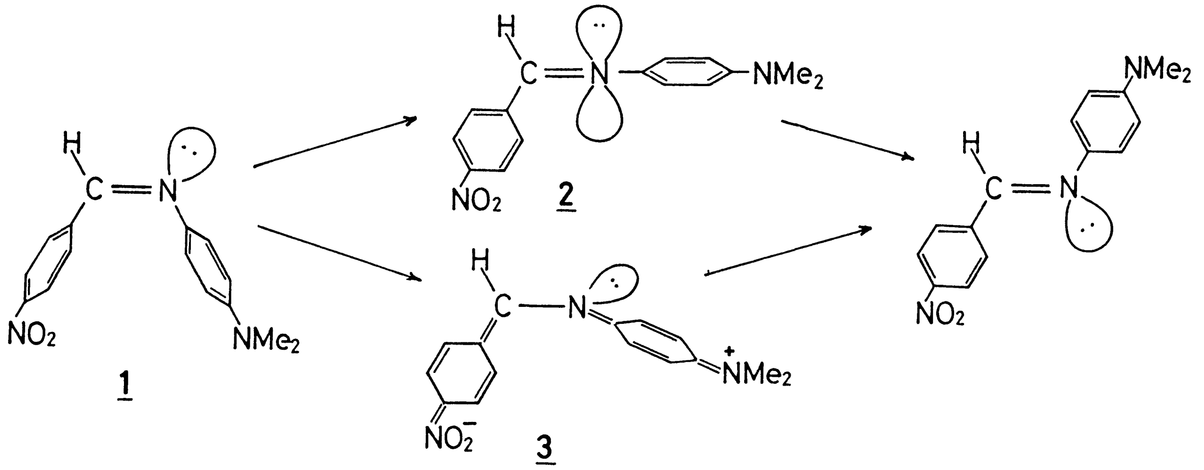
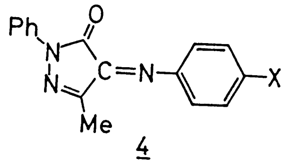
[†] This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.



Scheme 1.

isomerization about carbon-nitrogen double bond. Some ten years ago, Herkstroeter[6] reported that the Hammett plots for E-Z isomerization of pyrazolone azomethines (4) and other related compounds were V-shaped. The results can be explained most reasonably by the inversional mechanism for electron-attracting substituents (transition state 5) and the rotational mechanism for electron-donating substituents (transition state 6). A similar observation was reported recently by Prosyanik and his co-workers[7] for the degenerate isomerization of dimethyl malonate imines. By analogy with azobenzenes, the rotational transition states, 3 and 6, are expected to be much more polar than the initial state, and they must be characterized by stronger solute-solvent interactions. As proved in azobenzenes, an increase in polarity during activation is shown clearly by the large kinetic pressure effect. Therefore, we dicided to undertake pressure effect studies on N,N-dimethyl-N'-[(4-nitrophenyl)methylene]-1,4-benzenediamine (1) and 4-[[4-(dimethylamino)phenyl]-imino]-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (4a). The solvent effects in 4a at atmospheric pressure were also examined.



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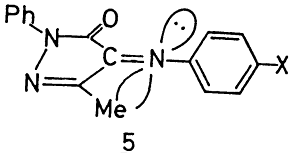
4a: X = NMe2



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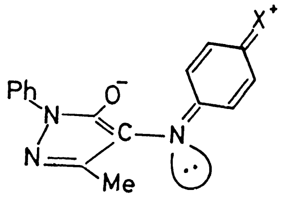

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The measurements were performed by means of high-pressure flash photolysis. The experimental details were reported elsewhere.[8] The first-order rate constants at different pressures are given in Tables 1 and 2. Figure 1 shows several representative results. Quite unexpectedly, the increase in pressure

Table 1. First-Order Rate Constants (k/s^{-1}) for Thermal Geometrical Isomerization of 1 and 4a at 25 °C and at Various Pressures

	Solvent					
	Hexane		Acetone		Methanol	
P/MPa	1	4a	1	4a	1	4a
0.1	0.511±0.021	28.1±0.5	0.245±0.021	16.7±0.3	0.0684±0.0049	14.9±0.5
30.0	0.509±0.026	27.4±0.8	0.220±0.043	16.0±0.4	0.0681±0.0049	14.3±0.5
60.0	0.496±0.024	27.0±0.6	0.225±0.024	15.3±0.4	0.0688±0.0074	13.6±0.5
90.0	0.501±0.024	25.9±0.5	0.192±0.053	14.7±0.4	0.0671±0.0082	13.0±0.4
120.0	0.494±0.022	25.4±0.8	0.218±0.032	13.9±0.2	0.0659±0.0035	12.4±0.4
150.0	0.497±0.025	24.6±0.5	0.205±0.039	13.1±0.4	0.0588±0.0088	11.8±0.5
180.0	0.497±0.031	23.6±0.5	0.201±0.031	12.7±0.4	0.0552±0.0077	11.3±0.4
210.0	0.498±0.019	23.4±0.6	0.231±0.064	12.2±0.4	0.0539±0.0059	11.0±0.4
240.0		22.6±0.5	0.199±0.023	11.7±0.4	0.0541±0.0082	10.6±0.4

Table 2. First-Order Rate Constants (k/s^{-1}) for Thermal Geometrical Isomerization of 1 and 4a in Benzene at 25 °C and at Various Pressures

P/MPa	0.1	20.0	40.0	60.0	70.0
1	0.248±0.014	0.248±0.024	0.248±0.019	0.234±0.020	0.243±0.020
4a	17.0±0.3	16.6±0.4	15.9±0.3	15.4±0.3	15.2±0.3

resulted in a slight decrease in the rate constant in all of the systems studied. The activation volumes were small but unmistakably positive. The values are given in Table 3. These results can not be reconciled with the highly dipolar rotational transition states, 3 and 6. The polarity of the reactant decreases slightly during activation. This conclusion is also supported by the results of solvent effect study at atmospheric pressure. As can be seen in Table 4, the solvent effect is small, but the rate constant clearly tends to decrease with the polarity of the solvent. The largest rate constant was obtained in hexane, and the smallest one was obtained

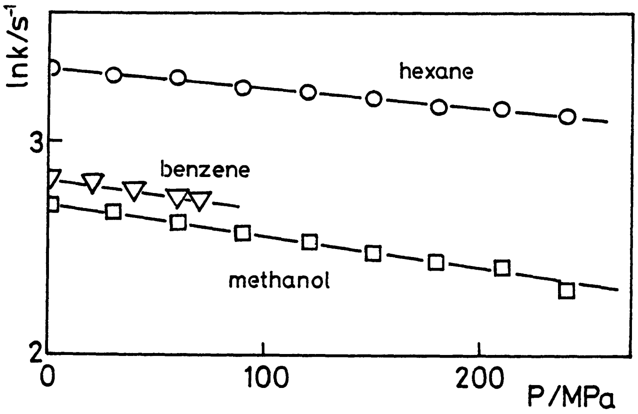

Fig. 1. Pressure effects on thermal E-Z isomerization of 4a at 25 °C.

Table 3. Activation Volumes (cm^3/mol) for Thermal Geometrical Isomerization of 1 and 4a at 25 °C in Various Solvents

	Hexane	Benzene	Acetone	Methanol
1	0.30±0.12	1.47±0.94	1.16±0.79	3.05±0.44
4a	2.30±0.09	4.17±0.18	3.72±0.08	3.59±0.09

Table 4. Kinetic Solvent Effects on Thermal E-Z Isomerization of 4a at 25 °C

Solvent	k/s^{-1}	Solvent	k/s^{-1}	Solvent	k/s^{-1}
Hexane	28.1±0.6	CH_2ClCH_2Cl	11.9±0.5	Formamide	7.10±0.2
Benzene	17.5±0.9	Acetone	17.1±0.4	*i*-PrOH	23.1±0.4
CCl_4	21.3±0.7	Cyclohexanone	16.0±1.7	Ethanol	19.7±0.7
$CHCl_3$	10.3±0.6	DMF	15.4±0.2	Methanol	14.4±0.3
CH_2Cl_2	10.9±0.1				

in formamide.

All of the results presented here strongly suggest that the mechanism of the geometrical isomerization about carbon-nitrogen double bond is inversional even in the presence of an electron-donating and -attracting substituents. Further measurements on other benzylideneanilines and pyrazolone azomethines are under progress and the results will be reported in the near future.

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