2598 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2598—2604 (1983) [Vol. 56, No. 9

Kinetic Pressure and Substituent Effects on the Thermal Isomerization of Triphenylformazans

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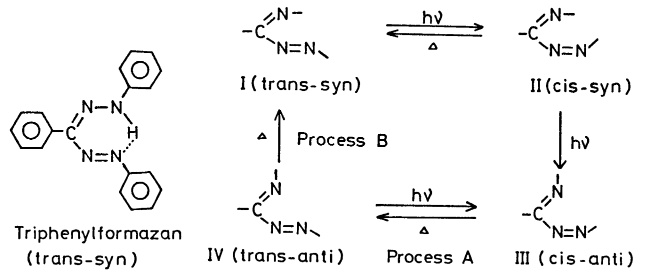
(Received April 2, 1983)

The rates of the thermal isomerizations around N=N (Process A) and C=N (Process B) of substituted triphenylformazans were followed spectrophotometrically at various temperatures and under high pressures, and the activation parameters were determined. The values of the activation energy, entropy, and volume were found to be *ca.* 70 kJ mol^{-1}, *ca.* -20 J K^{-1} mol^{-1}, and *ca.* -5.0 cm^3 mol^{-1} respectively for Process A, and *ca.* 40 kJ mol^{-1}, *ca.* -200 J K^{-1} mol^{-1}, and *ca.* -10 cm^3 mol^{-1} respectively for Process B. It was suggested that the thermal isomerizations both for Processes A and B proceed by the inversion mechanism. Furthermore, in the transition state of Process B, a quasi six-membered ring was assumed to form. The very large negative entropy of Process B was discussed in terms of the restricted internal rotations, and others.

Formazans have two double bonds. There are some reports with regard to their conformations and electronic and IR spectra.[1,2] However, there are very few reports regarding its isomerization mechanism. Kuhn and Weitz[3] suggested the following isomerization scheme.



Scheme 1.

But they did not give a full detail of mechanism of the thermal isomerization.

In the preliminary communication,[4] it was shown that the kinetic substituent effects really reverse above and below the isokinetic temperature. In spite of the low activation energy,[3] the rate of the thermal isomerization for Process B is so slow that it seems to us worth while investigating the reaction mechanism in some detail.

In analogy with the isomerizations of azobenzenes and azomethines, there are two possible mechanisms for the thermal isomerizations of triphenylformazans, one *via* a rotation around the double bonds and involves a π-bond rupture, the other *via* an inversion on the nitrogen atom, the π-bond remaining intact.[5,6]

This paper presents the substituent and pressure effects on the rate of the thermal isomerization of several formazans and their mechanistic implications are discussed.

Experimental

Reagents. Substituted triphenylformazans were prepared according to the method by Kuhn and Weitz[3] and recrystallized from a chloroform-ethanol mixture. Melting point and IR spectra were used for identification.

1,3,5-Triphenylformazan: mp 173 °C (lit, 173.5 °C), 3-(*p*-methoxyphenyl)-1,5-diphenylformazan: mp 157—158 °C (lit, 156—158 °C), 3-(*p*-methylphenyl)-1,5-diphenylformazan: mp 171—172 °C, 3-(*p*-chlorophenyl)-1,5-diphenylformazan: mp 199—200 °C (lit, 178—179 °C), 3-(*p*-bromophenyl)-1,5-diphenylformazan: mp 209—210 °C, 3-(*p*-cyanophenyl)-1,5-diphenylformazan: mp 221—222 °C, 3-(*p*-nitrophenyl)-1,5-diphenylformazan: mp 230—231 °C (lit, 204 °C), 3-(*m*-nitrophenyl)-1,5-diphenylformazan: mp 185.7 °C (lit, 185 °C), 1,5-bis(*o*-methylphenyl)-3-phenylformazan: mp 129—130 °C (lit, 130 °C, 1,5-bis(*p*-methylphenyl)-3-phenylformazan: mp 164—165 °C), 1,5-bis(*p*-chlorophenyl)-3-phenylformazan: mp 184—185 °C (lit, 183—184 °C).

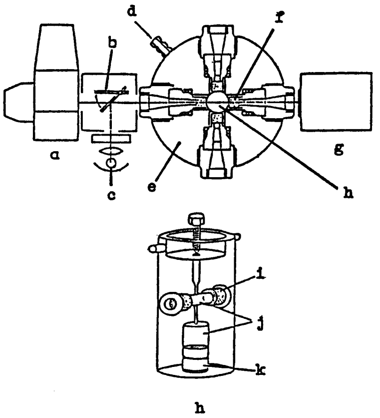


Fig. 1. Schematic diagram for spectrophotomeric measurement (top view) and inner cell.
a, Monochromator; b, turn mirror; c, tungsten lamp for excitation; d, water inlet; e, high pressure vessel; f, sapphire window; g, photomultiplier; h, teflon inner cell; i, sapphire window; j, sample cell; k, liquid separation piston.

Solvents. Toluene was dried over metallic sodium and distilled. Hexane of reagent grade was used as received.

Measurements under Atmospheric Pressure. An appropriate concentration of the sample solution was irradiated for 1 h with a 100W tungsten lamp to produce a *cis-anti* isomer (III). In the dark, the *cis-anti* isomer (III) isomerizes to a *trans-anti* isomer (IV) and the *trans-anti* isomer (IV) turns back to a *trans-syn* isomer (I) (Scheme 1), both in accordance with the first-order kinetics. The reaction rates for Processes A and B were estimated spectrophotometrically, by following the maximum absorbance at *ca.* 400 nm for the former by a Union 401 spectrophotometer, and the maximum absorbance at *ca.* 500 nm for the latter

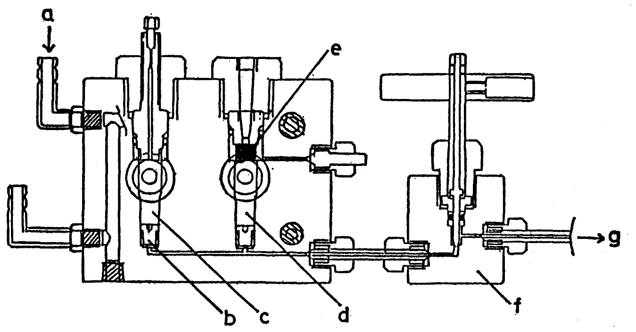


Fig. 2. High pressure vessel for spectral measurement (side view).
a, Water inlet; b, liquid separation piston; c, reference cell; d, sample cell; e, sapphire window for excitation light; f, stop valve; g, to pump system.

by a Hitachi 101 spectrophotometer. These are checked by several runs.

Measurements under High Pressures. The thermal *cis*-to-*trans* isomerization (Process A) was followed by using a pressure vessel made of SNCM-8 stainless steel and equipped with an inner cell, optical windows, and a water jacket (Fig. 1.). The pressure was generated by means of a plunger-pump. The pressure was measured by a Haise Bourdon gauge. The reaction temperature was controlled by circulating the thermostated water through the water jacket. Sample solutions were charged in the inner cell which is made of teflon and consists of two parts connected with a narrow tube, in order that an irradiated part of the solution for optical measurements does not mix with an unirradiated part of the solution. The solution was compressed, and then irradiated with a 650 W tungsten projection lamp for 1 min. After irradiation, the mirror b was turned by 45° and the change in the absorbance with time was followed with a Hitachi 139 spectrophotometer.

The rate of the thermal *anti*-to-*syn* isomerization (Process B) was so slow that this process was followed by using a high pressure vessel made of 17-4PH stainless steel (Fig. 2). The pressure vessel have two cells for sample and reference solutions, equipped with sapphire windows in horizontal direction for spectral measurements and one window in vertical direction for irradiation. The reaction solution in the pressure vessel was brought up to the required pressure, and then the stop valve was closed. The vessel was separated at the stop valve from the pump system. After the reaction solution had been irradiated with a 650 W tungsten projection lamp for 2 min, the pressure vessel was set in a Hitachi 100-50 double-beam spectrophotometer and the absorbance was recorded.

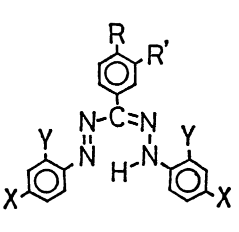
Results and Discussion

The thermal *cis*-to-*trans* and *anti*-to-*syn* isomerizations of substituted triphenylformazans were carried out at various temperatures. The rate constants estimated

TABLE 1. SUBSTITUENT EFFECTS ON RATE CONSTANTS, ACTIVATION ENERGIES, AND ACTIVATION ENTROPIES FOR THE THERMAL ISOMERIZATION OF PROCESS A IN TOLUENE (PROBABLE ERRORS IN PARENTHESES)

Compd No.	$10^2 k/s^{-1}$					E_a	$\Delta S^{\ddagger}_{298}$
	−5 °C	5 °C	15 °C	20 °C	30 °C	kJ mol^{-1}	J K^{-1} mol^{-1}
1	0.264(0.003)	0.926(0.007)	2.62(0.04)	4.57(0.06)	12.1(0.1)	74.9(1.7)	−22.6(6.7)
2	0.283(0.008)	0.914(0.009)	2.48(0.03)	4.12(0.13)	9.63(0.05)	64.5(1.7)	−59.8(6.3)
3	0.279(0.010)	0.902(0.002)		4.19(0.09)	11.0(0.8)	69.9(1.3)	−39.8(4.6)
4	0.261(0.002)	0.969(0.017)	2.01(0.07)	4.91(0.07)	15.2(0.5)	76.6(1.7)	−16.7(5.9)
5	0.256(0.004)	0.915(0.003)		5.09(0.07)	15.7(0.1)	78.7(1.3)	−8.8(4.2)
6	0.362(0.007)	1.10 (0.02)		5.79(0.08)		74.9(2.1)	−20.5(6.7)
7	0.376(0.004)	1.22 (0.02)		6.69(0.14)		74.1(0.8)	−22.6(2.9)
8	0.458(0.005)		3.53(0.04)	6.42(0.01)		71.5(2.1)	−33.5(6.7)
9	0.206(0.010)$^{a)}$	0.548(0.008)$^{b)}$	2.13(0.05)	3.60(0.05)	12.8(0.1)	80.8(1.3)	−5.0(4.6)
10	0.943(0.011)	3.65 (0.08)$^{c)}$		16.1 (0.3)		73.7(0.8)	−17.2(2.1)
11	0.417(0.004)	1.91 (0.07)$^{c)}$		8.11 (0.01)		77.4(2.5)	−10.0(9.6)

a) At −4.4 °C. b) At 4 °C. c) At 6.3 °C.



Compd No.	Substituent			
	R	R′	X	Y
1	H	H	H	H
2	OCH_3	H	H	H
3	CH_3	H	H	H
4	Cl	H	H	H
5	Br	H	H	H
6	CN	H	H	H
7	NO_2	H	H	H
8	H	NO_2	H	H
9	H	H	H	CH_3
10	H	H	CH_3	H
11	H	H	Cl	H

Table 2. Substituent effects on rate constants, activation energies, and activation entropies for the thermal isomerization of Process B in toluene (probable errors in parentheses)

Compd No.	$10^6 k/s^{-1}$ 25 °C	35 °C	40 °C	E_a kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$ J K^{-1} mol^{-1}
1	4.33(0.01)	6.39(0.49)	9.08(0.37)	36.9(4.3)	−231(14)
2	21.0 (0.3)	36.5 (0.7)	47.6 (3.2)	42.2(0.3)	−201(2)
3	14.8 (1.6)	26.1 (0.2)	27.5 (0.1)	33.7(5.7)	−232(19)
4	4.34(0.11)	9.94(0.04)	12.8 (2.1)	57.0(3.7)	−164(12)
5	5.38(0.37)	8.01(0.16)	11.5 (0.3)	37.9(4.5)	−227(15)
6	12.1 (1.2)	15.6 (0.4)	19.5 (1.3)	23.8(2.7)	−267(9)
7	10.8 (0.8)	23.8 (0.3)	41.8 (3.5)	68.5(4.9)	−119(16)
8	28.1 (0.6)	65.1 (8.1)	66.9 (2.8)	47.8(9.8)	−179(32)
9	2.44(0.06)	9.34(0.79)	13.9 (1.6)	91.8(6.3)	−52(21)
10	19.3 (0.9)	40.2 (3.7)	51.2 (0.5)	51.2(2.8)	−171(9)
11	3.92(0.35)	5.07(0.50)	6.02(0.40)	21.8(1.3)	−283(4)

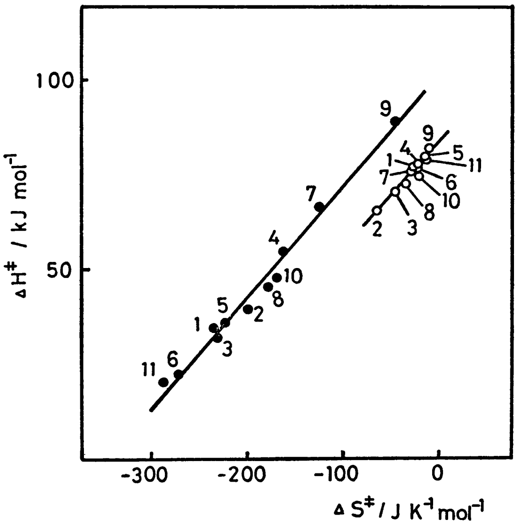


Fig. 3. $\Delta H^{\ddagger}-\Delta S^{\ddagger}$ relationships for Processes A (○) and B (●).

from the first-order plots and the activation parameters are listed in Tables 1 and 2. It is interesting to note that the activation entropies for Process B are surprisingly small except **9**. Therefore, the rate constants for Process B are about 10^4 smaller than those for Process A, in spite of the very low activation energies. In **9**, the steric effect by the *ortho*-CH_3 substituent may be severe in the transition state and this may be responsible for both the increased activation energy and entropy. Figure 3 shows the linear relationships between the activation enthalpy and entropy. This linear enthalpy-entropy relationship suggests that in Process B as well as A, a single mechanism is operating.[7] Similarly, a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ has been reported for the thermal *cis*-to-*trans* isomerization of substituted azobenzenes.[8]

Arrhenius Parameters. It has been shown theoretically that the activation energies for the *syn*-to-*anti* isomerization of oximes[9–12] by the inversion mechanism are lower than those by the rotation mechanism. Moreover, Warren *et al.*[13] calculated the energy barrier for the isomerization of *N*-benzylideneaniline *via* the inversion to be 88.8 kJ mol^{-1} and the barrier to the rotation around the C=N double bond was calculated to be 252 kJ mol^{-1} by means of the CNDO/2 method. Experimental values of various kinds of azobenzenes and azomethines are about 80 kJ mol^{-1}. Most of the activation entropies for the thermal isomerizations of azobenzenes and azomethines fall in the range of about −60 to 0 J K^{-1} mol^{-1}. Judging from these, our results for Process A (Table 1) seem to be compatible with the inversion mechanism.

Recently, Bach and Wolber[9] reported that electron-withdrawing substituents at nitrogen markedly increase the inversion barrier and that an allyl type molecular orbital containing the nitrogen lone pair contributes most significantly to the activation energy. On the other hand, it has been suggested that if substituents at carbon strongly polarize the π-electron of the C=N bond, the rotation mechanism accompanying the charge separation might be possible.[10,14] Moreover, Bauer *et al.*[15] and Taylor and Bartulin have reported that the activation energies for the rotational isomerizations of guanidine salts around the C=N bond and of some olefines around the C=C bond are as low as 80 kJ mol^{-1} or even less. Therefore, the activation energy less than 80 kJ mol^{-1} may not necessarily afford a conclusive evidence for the inversion mechanism.

The extraordinarily small values of the Arrhenius parameters for Process B (Table 2) are noteworthy. There are some examples of such small values of the activation entropy for second-order reactions. As far as we are aware, however, the values of the activation entropy for first-order reactions are much larger than this. The above findings have lead us to the idea that the transition state might be much more product-like and hence its molecular conformation is similar to that of *trans-syn* for which a quasi six-membered ring is formed, internal rotations being severely restricted.

Since an internal rotation interacts with other modes of rotations and vibrations, it is difficult to calculate the exact contribution of the internal rotation to entropy. However, if we use a proper model, the rotational entropy can approximately be estimated. Figure 4 shows a model of the cyclic transition state of triphenylformazan. If a quasi six-membered ring for-

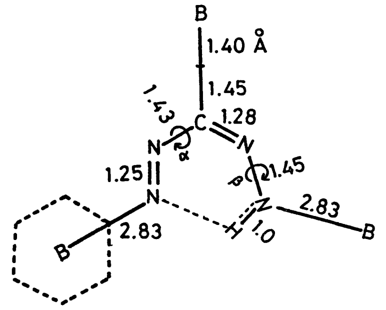


Fig. 4. Model of the cyclic transition state of triphenylformazan. The bond lengths (Å) of azobenzene derivative[17] and *N*-benzylideneaniline[13] were used. B, Phenyl group; C, carbon; N, nitrogen; H, hydrogen.

mation occurs in the transition state, rotations around the C–N and N–N bonds as depicted become impossible. Now, for brevity, we assume that the two possible internal rotation axes agree with these bond-axes. The entropy of an internal rotation can be calculated by

$$S_{\rm rot} = NkT(\mathrm{d}\ln q_{\rm rot}/\mathrm{d}T) + Nk\ln q_{\rm rot}, \qquad (1)$$

where $q_{\rm rot}$ is the one-dimensional rotational partition function and is given by

$$q_{\rm rot} = (8\pi^2 IkT/h^2)^{1/2}\pi^{1/2}/\sigma, \qquad (2)$$

for which σ is the symmetry number and the reduced moment of inertia I is given by $I=I_1I_2/(I_1+I_2)$ in which I_1 and I_2 are the moment of inertia around the common axis. Therefore, $S_{\rm rot}$ is expressed as follows.

$$\begin{aligned} S_{\rm rot} &= Nk\left[\frac{1}{2}+\frac{1}{2}\ln(8\pi^3 IkT/h^2)-\ln\sigma\right] \\ &= R\left[\frac{1}{2}\ln(I/\text{amu Å}^2)+\frac{1}{2}\ln(T/\text{K})-\ln\sigma-0.522\right]. \qquad (3) \end{aligned}$$

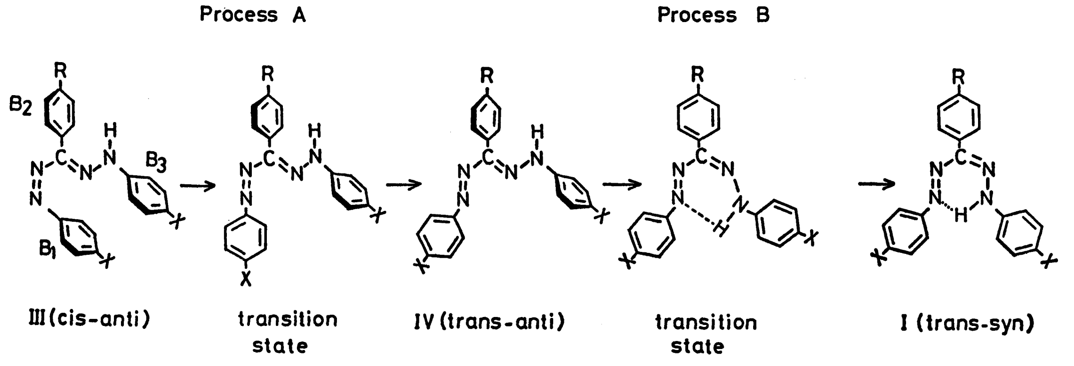
Substituting the numerical values into these equations, the entropies for the internal rotations around the C–N and N–N bonds at 25 °C are calculated to be $S_{\rm rot}$(C–N)=38.6 J K^{-1} mol^{-1} and $S_{\rm rot}$(N–N)=44.1 J K^{-1} mol^{-1}. Therefore, the total entropy loss due to these restricted rotations may be about 80 J K^{-1} mol^{-1} on going from the initial to the transition state.

It may be instructive to compare the entropy loss with those of similar reactions. For example, some Claisen and Cope rearrangements[18,19] have been reported to proceed *via* a cyclic transition state. The entropies of activation for the Claisen rearrangement of allyl ethers have been reported as −50—−120 J K^{-1} mol^{-1}.[18] Assuming that only two rotations around the O–CH$_2$ and CH$_2$–CH bonds become forbidden upon activation, the total entropy losses for the corresponding species can be estimated as −50—−90 J K^{-1} mol^{-1}. For 3-phenyl-2-propenyl phenyl ether, the discrepancy is *ca.* 30 J K^{-1} mol^{-1} probably owing to the restriction of other modes of internal rotations involving two phenyl rings upon activation.

Now, in our case, the steric hindrance in the transition state may become less severe than in the ground state, and hence one might imagine that the free rotations involving the benzene rings become possible (see Scheme 2). However, as we have advocated in the case of the thermal isomerization of azobenzenes,[5] the most important factor for determining the conformation of such a "soft" species involving aromatic rings connected by single bonds is mesomeric one. Therefore, the mesomeric effects which tend to keep the three benzene rings coplanar would overwhelm the tendency for them to rotate freely, resulting in the net loss of entropy upon activation. Indeed, the absorption maxima of the conjugation band are 495 nm for the *trans-syn* isomer (I) and 405 nm for the *trans-anti* isomer (IV), suggesting a drastic change in the molecular conformation (coplanality).

There is a vast of reports for hydrogen bond formation.[20] The reported values of ΔH and ΔS for the H-bond formation vary depending on the type of bonding and others, but ΔH is generally *ca.* −20 kJ per H-bond per mol, and ΔS is *ca.* −50 J K^{-1} mol^{-1}. If the H-bond formation takes place in the transition state for Process B, further entropy loss of *ca.* 50 J K^{-1} mol^{-1} could be expected. The contribution from the solvation may be responsible for at least a part of the remaining entropy loss.

The very low values of the activation energy for Process B (Table 2) seem to be worth to pay attention. According to the Hammond postulate, among a group of similar reactions, the less exothermic ones have the later transition states and *vice versa.* Since Process B involves a formation of the hydrogen bond, it must be exothermic ($\Delta H\approx-20$ kJ mol^{-1}, *vide supra*). At first sight, it seems that the reaction may have the earlier transition state compared with similar types of isomerizations, and this is apparently against the



Scheme 2.

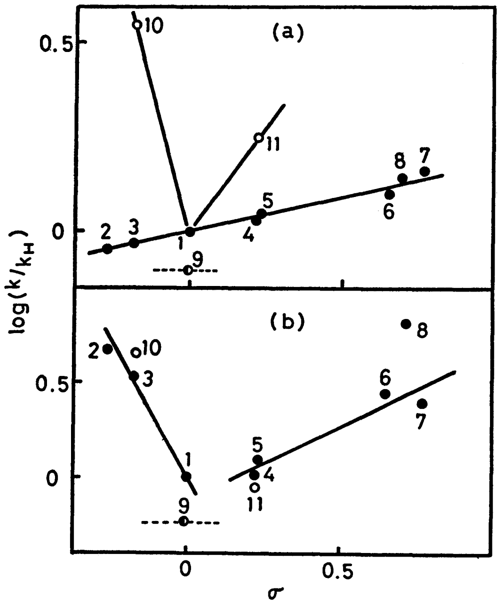
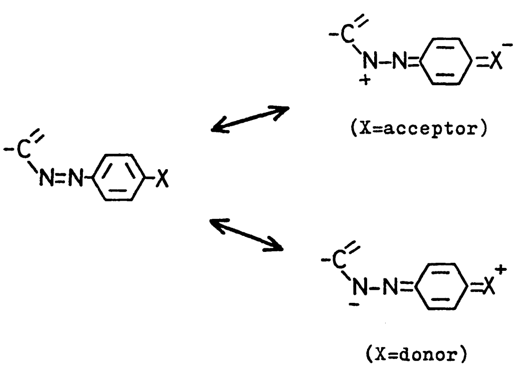


Fig. 5. Plots of log (k/k_H) against the Hammett σ for (a) Process A at 20 °C and (b) Process B at 25 °C. ●: Substituents R, ○: substituents X, ◐: **9**.

above assumption that the conformation of the transition state is similar to I. However, as seen above, the entropy factor plays a very important role in this process, and the reaction is controlled by the activation energy as well as the activation entropy. The isokinetic temperature (*ca.* 300 K) estimated from the slope of the linear ΔH^* *vs.* ΔS^* plot in Fig. 3 is very near the experimental temperatures. In such a case as this, the Hammond postulate must be invalidated, since the postulate tacitly assumes that reactions in question are energy-controlled. It is noted that the true reaction coordinate must be drawn in terms of the free energy. Therefore, in spite of the low activation energy, the barrier of the free energy will be at the later stage of reaction coordinate.

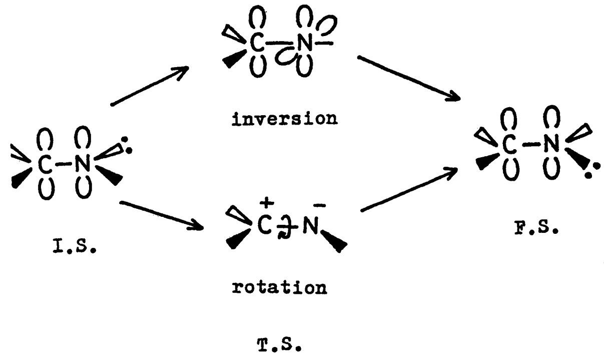
Substituent Effects. In the preliminary communication,[4] we reported that the strictly linear ΔH^*–ΔS^* relationship holds for a limited series of substituted triphenylformazans and the isokinetic temperature at which substituent effects should vanish does exist (Process A). Figure 5(a) shows the substituent effect for the thermal isomerizations of 11 kinds of triphenylformazans. The Hammett plots of **1**, **10**, and **11** show a V-line. Moreover, the *ortho*-substituent retards the isomerization rate (**9**). On the other hand, a linear Hammett relationship approximately holds for **1**—**8**. The above findings are considered as follows. In the *cis-anti* conformation, the three benzene rings (B_1, B_2, and B_3 in Scheme 2) must be twisted to one another owing to the steric repulsion (III in Scheme 2). In the inversion transition state, however, a conjugation between the reaction center (the N=N bond) and the substituent X in B_1 becomes possible, thus resulting in the extra free energy depression in analogy with the case of azobenzene derivatives,[5] as depicted in Scheme 3:



Scheme 3.

The acceleration effect irrespective of the nature of substituents is accounted for by this reason. On the contrary, in **1**—**8**, a conjugation of the reaction center (the N=N bond) and the substituent R in B_2 is impossible. Therefore, the substituent R would exhibit a mild inductive effect, thus accounting for the usual Hammett relationship. In the rotational mechanism, these substituent effects can be explained in no way.

There are two possible routes also for Process B (Scheme 4).



Scheme 4.

The isomerizations of azomethines[20,21] are also characterized by a V line. Herkstroeter[21] and Hall *et al.*[22] explained the V plot in terms of the change in mechanism. As explained earlier,[4] we have a different idea. If the inversion transition state is assumed for Process B, B_2, B_3, and the connecting C=N–N group would become coplanar. This makes the conjugation between the substituent R and the C=N–N group possible, but the conjugation between the substituent X and the C=N group is impossible. Therefore, the kinetic behavior of a series of the substituents R (the V plot in Fig. 5(b)) and of X can well be accounted for by the same way as explained for Process A. On the contrary, if the rotational transition state is assumed, the introduction of the electron-donating groups (R) would help the polarization (Scheme 4) and hence the isomerization rate is accelerated and *vice versa*. Thus we may expect the linear Hammett plot. This is against the experimental observations. The detail of the discussion on this problem has been reported elsewhere.[5]

Pressure Effects. The entropy of activation often affords important informations about the manner of

Table 3. Pressure effects (k_p/k_1) and activation volumes for Processes A and B

	Compd No.	Solvent	Temp °C	$P/10^5$ Pa	k_p/k_1 1	230	390	540	770	790	1180	ΔV^{*} cm³ mol⁻¹
Process A	**1**	Toluene	15		1		1.09			1.17	1.29	−5.0±0.1
	2	Toluene	15		1		1.08			1.17	1.25	−4.5±0.1
	7	Toluene	15		1		1.07			1.16	1.26	−4.7±0.1
Process B	**1**	Toluene	20		1	1.17	1.13	1.17	1.39			−8.7±1.4
	1	Hexane	45		1		1.18			1.47	1.66	−11.7±0.6
	3	Hexane	45		1		1.13			1.36	1.61	−10.9±0.5
	7	Hexane	45		1		1.14			1.23	1.50	−8.6±0.7

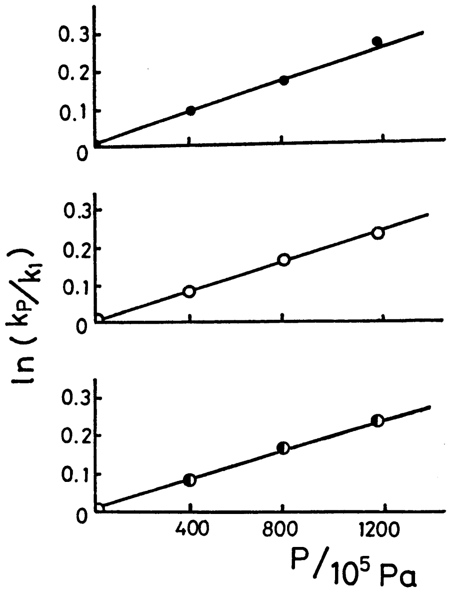


Fig. 6. Pressure effects on the thermal isomerization for Process A in toluene at 15 °C.
●: **1**, ○: **2**, ◐: **7**.

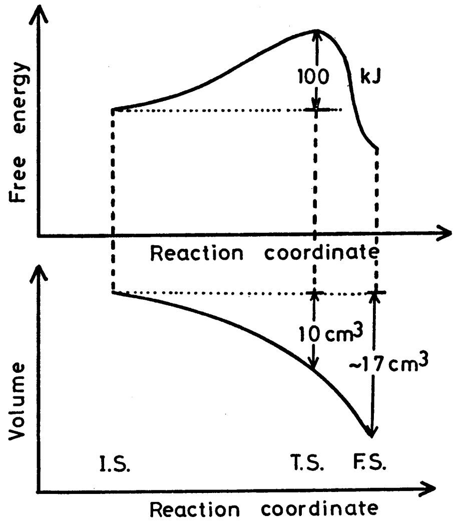


Fig. 7. Free energy and volume profiles for Process B.

bonding, the change in freedom, the extent of solvation, *etc.* However, since ΔH^{*} and ΔS^{*} can be obtained as a set from the Arrhenius plot, inevitable errors are often involved in ΔS^{*}, which, as pointed out by Petersen,[23] might lead to the misunderstanding for the existence of the isokinetic temperature. On the other hand, the volume of activation can be estimated from the slope of ln *k versus P* plot, in accordance with Eq. 4,

$$(\partial \ln k/\partial P)_T = -\Delta V^{*}/RT, \tag{4}$$

and the concept of volume is more straightforward than that of entropy. The activation volume is usually divided into two terms:

$$\Delta V^{*} = \Delta V_1^{*} + \Delta V_2^{*}, \tag{5}$$

where ΔV_1^{*} represents the difference in the intrinsic volume of reacting molecules between the initial and the transition state, and ΔV_2^{*} is the change in volume of surrounding solvents. Therefore, if no substantial intrinsic volume change is expected as may be so for Process A, ΔV^{*} obtained experimentally may be ascribed to ΔV_2^{*}.

Pressure effects on the thermal isomerizations for Processes A and B are given in Table 3. The rate constants in logarithmic scale were plotted against *P* (Fig. 6), and the estimated activation volumes are given in Table 3.

The small negative values of the activation volume for Process A indicate that the polarity change is, if any, not so large as suggested for the rotational transition state.[24] These values are, together with the values of E_a and ΔS^{*}, very similar to those for the isomerization of azobenzene derivatives for which the inversion mechanism has been advocated.[5,8]

Judging from the very small activation entropy for Process B, the transition state might be highly polar. However, the activation volume indicates that it is not so. If the isomerization for Process B proceeds *via* a cyclic transition state, the activation volume may be similar to those of the Claisen and Cope rearrangements.[25,26] The activation volumes reported are −9—−18 cm³ mol⁻¹ for these reactions, and are −9.5 ($\alpha \rightarrow \gamma$) and −7.9 ($\gamma \rightarrow \alpha$) cm³ mol⁻¹ for the equilibration of α- and γ-methylallylazide[27] respectively. It has been considered that these reactions proceed *via* moderately polar cyclic transition states. Judging from the values in Table 3, the isomerization for Process B will proceed *via* a moderately polar and cyclic transition state. It may safely be considered that the difference in the molar volumes between the *trans-syn* isomer (I) and the *trans-anti* isomer (IV) is similar to that between 1-hexene and cyclohexane (−17 cm³ mol⁻¹).[26] On the basis of the activation parameters and on the assumptions stated above, the presumed free energy and volume profiles for Process B could be sketched as shown in Fig. 7.

In conclusion, the kinetic substituent and pressure effects, together with the activation parameters, are in favor of the inversion mechanism *via* the moderately polar transition states both for Processes A and B, and against the rotational mechanism *via* the very polar transition states.

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