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A DEMONSTRATION OF THE EXISTENCE OF ISOKINETIC TEMPERATURE IN THE THERMAL ISOMERIZATION OF TRIPHENYLFORMAZANS

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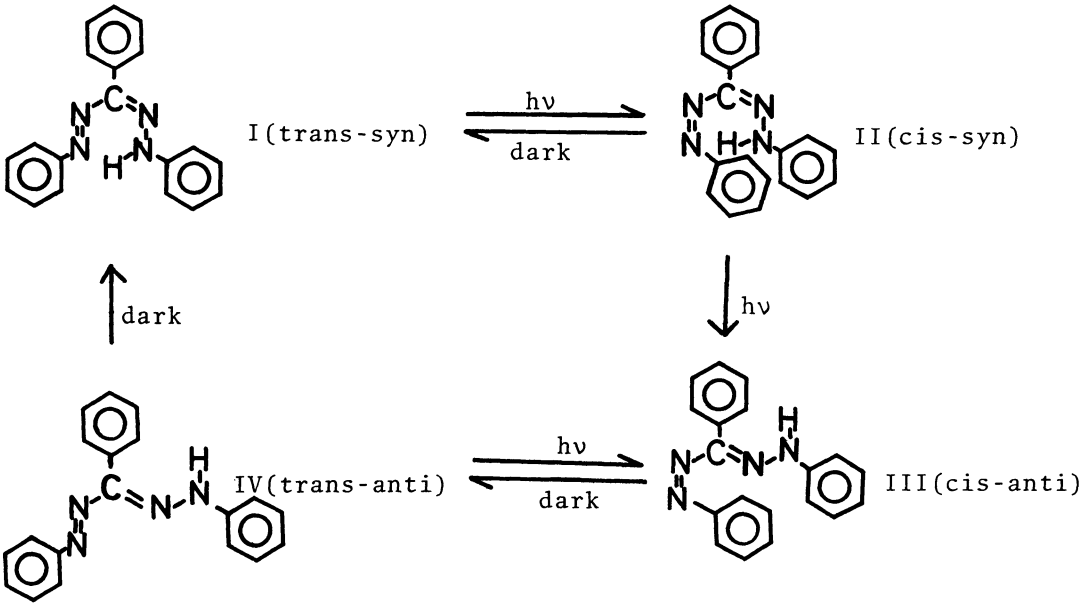
Substituent effects on the rate of the thermal isomerization of triphenylformazans have been studied at various temperatures. Strictly linear $\Delta H^{\ddagger}$–$\Delta S^{\ddagger}$ relationship was found to hold for a limited series of compounds. The isokinetic temperature β was calculated to be 281K from the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ plot. Reversal in the rate for these compounds was observed above and below this temperature.

Triphenylformazan has four types of molecular conformations and following isomerization scheme has been proposed by Kuhn and Weitz.[1]



We have been interested in the mechanism of isomerization of azobenzenes[2,3] and azomethines.[4] In relation to these compounds, the isomerization of triphenylformazan attracted our interest, since this substance has a -N=N- and a >C=N- group.

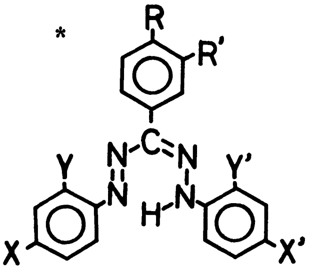
A toluene solution of I(ca. 10^{-4}M) was irradiated for 30 min. with a 30W tungsten lamp(the light was collimated by a lens and the UV-region was cut by a glass filter).

Then a mixture of III and IV was obtained. In the dark, III isomerizes to IV and IV turns back to I, both in accordance with the exact first-order kinetics. Since the process III ⟶ IV takes place about one hundred times faster than the process IV ⟶ I, these two processes could be followed independently. Rate constants for the former process were estimated by following the absorbance at ca. 405 nm by a spectrophotometer. These were checked by several runs and the mean values are listed in Table 1.

Table 1. Kinetic Data and Arrhenius Parameters for the Process III ⟶ IV (Probable Errors in Parentheses)

Compound	Substituent*				10^2k(20°C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$(298K)
	R	R'	X, X'	Y, Y'	(sec^{-1})	(kcal/mol)	(cal/mol)
1	H	H	H	H	4.57(0.06)	17.4(0.4)	-5.4(1.6)
2	OCH_3	H	H	H	4.12(0.13)	14.9(0.4)	-14.3(1.5)
3	CH_3	H	H	H	4.19(0.09)	16.2(0.3)	-9.5(1.1)
4	Cl	H	H	H	4.91(0.07)	17.8(0.4)	-4.0(1.4)
5	Br	H	H	H	5.09(0.07)	18.3(0.3)	-2.1(1.0)
6	CN	H	H	H	5.79(0.08)	17.3(0.5)	-4.9(1.6)
7	NO_2	H	H	H	6.69(0.14)	17.2(0.2)	-5.4(0.7)
8	H	NO_2	H	H	6.42(0.01)	16.5(0.5)	-8.0(1.6)
9	H	H	H	CH_3	3.60(0.05)	18.8(0.3)	-1.2(1.1)
10	H	H	CH_3	H	16.1(0.3)	17.0(0.2)	-4.1(0.5)
11	H	H	Cl	H	8.11(0.01)	17.9(0.6)	-2.4(2.3)

*



In Fig. 1, $\Delta H^{\ddagger}$ is plotted against $\Delta S^{\ddagger}$. The substituent effects on the rate of isomerization, the numerical values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and approximate linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, all support that III isomerizes to IV via inversion mechanism.[2,3] The effects of R and R' on the rate are very small compared with those of X, X', and Y, Y'. This could be explained in terms of inductive and mesomeric concepts. A scatter in Fig. 1 may indicate that the multiple interaction mechanism[5] is operative.

During the inspection of the points in Fig. 1, we noticed that five points just fall on a straight line, the correlation coefficient r being 0.999. The reason why this exact linear relationship holds only for these limited series of compounds is

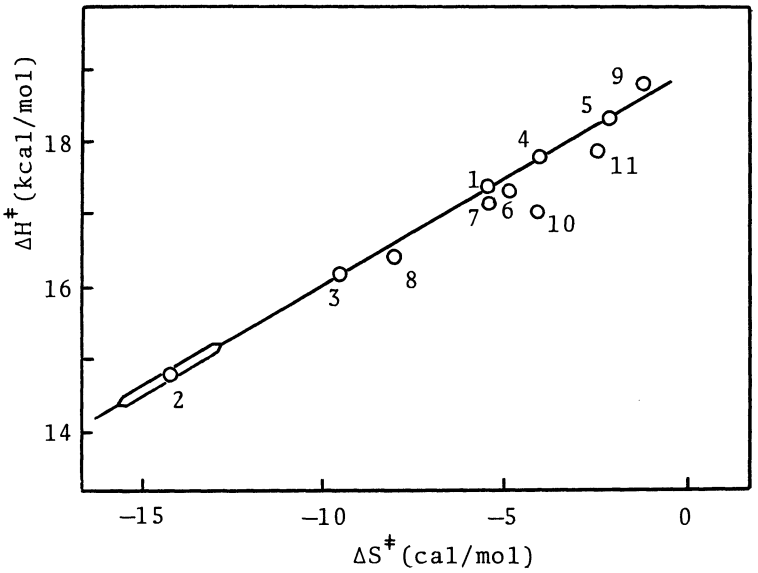


Fig. 1. Activation enthalpy vs. entropy for the process III ⟶ IV. Key is shown in Table 1. A probable error contour[5)] for 2 is indicated.

not clear for the time being. From the slope in Fig. 1 the isokinetic temperature β at which substituent effects should vanish was calculated to be 281K.

According to the theory of absolute reaction rates, the rate constant of a reaction is related to the free energy of activation $\Delta G^{\ddagger}$ which may be governed by some intensity factors χ_1, χ_2...If in a series of reactions one of the intensity factors affects $\Delta G^{\ddagger}$ linearly, i. e., $\partial \Delta G^{\ddagger}/\partial \chi$ = const., while other factors do not, $\Delta H^{\ddagger}$ should vary in such a way that $\Delta S^{\ddagger}$ is linearly related to it. It should be emphasized that this is a requirement of the thermodynamic relationship $\Delta G^{\ddagger}=\Delta H^{\ddagger}-T\Delta S^{\ddagger}$. As appropriate χ's, we may choose pressure P, ionic strength μ(operating form is $\mu^{1/2}$ for ionic reactions for example), dielectric constant ε(operating form: $1/\varepsilon$ ··), Y- and Z-values ...(external), and various σ's of the Hammett type(internal). The choice depends on the condition under which work is undertaken.

So many examples have been given for the linear free energy relationship and discussed in detail by Leffler.[5,6)] However, Petersen[7)]questioned the validity of the relationship. He stated that errors in estimating $\Delta H^{\ddagger}$ invariably give rise to the error in $\Delta S^{\ddagger}$ and therefore, an apparent linear enthalpy–entropy plot can be extremely deceptive and is not by itself an adequate demonstration of the existence of the isokinetic temperature. Usually, working temperatures are far below or far above the isokinetic temperature and therefore, it could be very rarely realized. As far as we are aware, no work on the substituent effects on reaction rates seems to have been done above as well as below β.

In Fig. 2, log k/k_H is incidentally plotted against the Hammett σ. It is noteworthy that in the vicinity of β(281K), the substituent effects do vanish, and above and below this temperature, the rates are really reversed. The above findings show that the simple interaction mechanism is operative for this series of compounds, although it has not been substantiated. The fact that the Hammett relationship is obeyed only approximately is not surprising, since the Hammett σ(para) involves both mesomeric and inductive effects(multiple interaction). The temperature dependence of ρ has been discussed elsewhere.[5,8)] From the ρ vs. 1/T plot, β was calculated to be 276K which agrees well with that obtained from the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ plot.

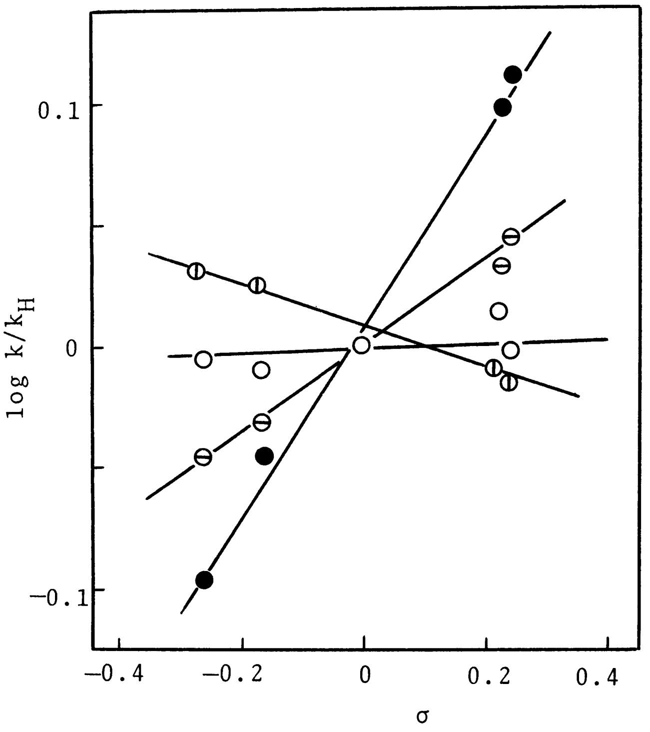


Fig. 2. Plots of log k/k_H against the Hammett σ.

—●— 30°C
—⊖— 20°C
—○— 5°C
—⦶— -5°C

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