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# The Isokinetic Relationship.
# VII. Statistical Analyses and Examples for Unimolecular Reaction Systems

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## Abstract

The existence of the isokinetic relationship (IKR), also called the 'compensation effect', is examined for unimolecular reaction series. A statistical analysis on the bases of a common point of intersection of the Arrhenius plots is given. This method is performed using three experimental examples. They exhibit highly precise IKRs, showing that this relationship is not necessarily an artefact based on measurement errors. The isokinetic temperature, $T_{iso}$, of a reaction series is significantly higher in an excess of a monoatomic inert gas than in gas phase reactions without the inert gas or for reactions in condensed phase. The isokinetic temperature seems to correspond to energy quanta available in the system which can be found in the vibrational spectra of the system.

## 1. Introduction

One of the favorite pastimes of many chemists is to think in terms of homologous (in the widest sense of the word) series and to seek linear relationships within such series. It might be argued in fact that without such 'linear group' thinking chemistry would have developed in a very different way. One of these 'linear' topics, the isokinetic relationship (IKR), has led to a lot of misunderstandings and controversies [1–11]. The IKR [12] has also been called the 'compensation effect' [13], the $\theta$-rule [14], the isoselectivity relationship [15], the Zawadzki–Bretsznajder rule [16], etc. It was originally expressed as a proportionality between entropic and enthalpic parameters within a series of similar or homologous reactions [5, 6, 17]. A computer search in Chemical Abstracts using the above key words gave some three hundred references, which are almost all of experimental character. Although mentioning the effect most of the papers are not based on a proper statistical analysis either to accept or to reject the existence of the IKR in each case. Assuming that there are a lot more papers containing temperature dependent rate or equilibrium constants (the effect is reflected in both kinetic and thermodynamic data [5, 12]) which might be analysed for their IKR behavior it seems worthwhile to investigate this problem in detail.

One of the problems that arises when discussing effects such as the IKR, is to convince oneself that they are in fact real [1–5, 7, 14]. Two reasons exist for this state of affairs; firstly many (insufficient) statistical analyses have been used to establish IKRs, and on this basis they can readily be discredited [7, 10, 18]. Secondly there seems to exist no general or common accepted theory [5, 11, 19] that would give the IKR respectability by providing a physical interpretation of its characteristic parameters. Besides models restricted to very special cases, in catalysis as induced by surface phase transitions [14], or by heterogeneous surfaces with different activity [20], a general explanation of the IKR has been provided by Conner [21, 22] that relates the 'availability' and 'accessibility' of energy to the kinetic compensation that is often found.

The primary complication (which is crucial to the whole matter) is that enthalpy–entropy proportionalities may occur artificially [5, 8, 9] due to the (experimentally caused) mutual dependence of the specific parameters [10, 11]. In our initial analysis of these phenomena we have developed a statistical approach to analyse the available data [18]. This method is given in a developed form in section II and is applied to experimental data in section III. The main purpose of the present paper is to show with experimental data available that the IKR is not necessary an artefact. A statistical mechanical model presented in the first two parts [1, 2] of this seires will be applied in section IV to the reaction series where compensation has been proposed. However, this should provide the experimental basis for a detailed theoretical investigation presented in parts V, VI and VIII of this series [23–25].

## II. The Statistical Analysis of the IKR

As pointed out elsewhere [6, 10, 18] the IKR has originally been analyzed by means of a linear relation-

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ship between $\Delta H$ and $\Delta S$. Both are usually calculated from the slope and intercept of the Arrhenius or van't Hoff plot and therefore cannot be treated as statistically independent variables, as is required for a linear regression analysis. The pitfall of such a procedure is illustrated by looking at the data from the isomerization of a series of triphenylformazanes (see section III,3). However, statistical methods to decide whether a reaction series is isokinetic in character are available and should be a fundamental tool for investigating the temperature dependence of reaction series.

There are two main statistical procedures for analysing the existence of an IKR from given data. The procedure of Krug [10], which is based on a variation analysis of a $\Delta G$ *versus* $\Delta H$ relation, and a procedure based on the work of Exner [5,11] showing that a common point of intersection exists in the Arrhenius or van't Hoff plot (or any other plot of straight lines which should be analysed in terms of an isoparametric relationship [3,4,18]. In our opinion the use of a slightly modified Exner method is much to be preferred as it gives (in contrast to the Krug test) the position of the characteristic parameters of the IKR (*i.e.* the isokinetic temperature and the isokinetic rate or equilibrium constant) strictly. Furthermore this test is not restricted to numbers and values of the temperatures at which the members of the series are measured. A statistical analysis based on the original approach used by Exner [5,11] is somewhat modified to enable $F$ tests and is described in the following. However, for data sets where both methods can be applied, they yield in general similar results. It should be pointed out that the method given below performs the strongest test for the existence of the IKR of all methods available.

For a given set of straight lines in the Arrhenius plot (or arbitrary plots to be investigated like van't Hoff plots, Hammett plots, and other LFERs) the common point of intersection is calculated at an arbitrary position along the abscissa (*i.e.* at a specific value of the reciprocal temperature represented as $x = 1/RT$ with the isokinetic temperature given by $1/RT_{\mathrm{iso}} = x_{\mathrm{iso}}$). For this point the sum of squares of the deviations of the measurement points from the corresponding straight line, including this point of intersection $S_x$, is calculated. These are called constrained lines. By varying the common point of intersection along the abscissa (the $1/T$ axis), the minimum of $S_x$ is calculated and denoted by $S_0$. By means of an $F$ test this value (somewhat modified to get a nearly $F$ distributed variable) is compared with the sum of deviations of the measurement points from the unconstrained lines $S_{00}$. In detail $S_x$, $S_{00}$, $y$ (equal to $y_{\mathrm{iso}}$ for $S_x = \mathrm{Min!}$) and the $\bar{F}$ value to be compared with the corresponding $F$ value from the table are given by:

$$y = \frac{\displaystyle\sum_{ij} y_{ij} - \sum_i \frac{\left(\sum_j x_{ij} - m_i x\right)\left(\sum_j x_{ij} y_{ij} - x \sum_j y_{ij}\right)}{\sum_j x_{ij}^2 - 2x \sum_j x_{ij} + m_i x^2}}{\displaystyle\sum_i m_i - \sum_i \frac{\left(\sum_j x_{ij} - m_i x\right)^2}{\sum_j x_{ij}^2 - 2x \sum_j x_{ij} + m_i x^2}} \tag{1}$$

$$S_x = \sum_{ij} y_{ij}^2 + l y^2 - \sum_i \frac{1}{m_i + 1}\left(\sum_i y_{ij} + y\right)^2 - \sum_i \frac{\left[\sum_j x_{ij} y_{ij} + xy - \frac{1}{m_i + 1}\left(\sum_j x_{ij} + x\right)\left(\sum_i y_{ij} + y\right)\right]^2}{\sum_j x_{ij}^2 + x^2 - \frac{1}{m_i + 1}\left(\sum_j x_{ij} + x\right)^2} \tag{2}$$

$$S_{00} = \sum_{ij} y_{ij}^2 - \sum_i \frac{1}{m_i}\left(\sum_j y_{ij}\right)^2 - \sum_i \Bigg[ \Bigg( \sum_j x_{ij} y_{ij} - \frac{1}{m_i} \sum_i x_{ij} \sum_j y_{ij} \Bigg)^2 \Bigg/ \Bigg\{ \sum_j x_{ij}^2 - \frac{1}{m_i}\left(\sum_j x_{ij}\right)^2 \Bigg\} \Bigg] \tag{3}$$

$$\bar{F} = \{(S_0 - S_{00})/f_1\}(f_2/S_{00}) \tag{4}$$

$$S_\infty = \sum_{ij} y_{ij}^2 - \sum_i \frac{1}{m_i}\left(\sum_j y_{ij}\right)^2 - \Bigg[ \Bigg\{ \sum_{ij} x_{ij} y_{ij} - \sum_i \frac{1}{m_i}\left(\sum x_{ij}\right)\left(\sum y_{ij}\right) \Bigg\}^2 \Bigg/ \Bigg\{ \sum_{ij} x_{ij}^2 - \sum_i \frac{1}{m_i}\left(\sum_j x_{ij}\right)^2 \Bigg\} \Bigg] \tag{5}$$

In this expression $x$ and $y$ are the coordinate axes ($x = T^{-1}$, $\sigma$, etc; $y = \ln k$, $\ln K$, etc.), $m_i$ the number of points per straight line $i$; $l$ the number of such straight lines and $f$ statistical degrees of freedom, $f_1 = l - 1$ and $f_2 = \Sigma_i m_i - 2l$. The curved lines in Figs. 1–6 represent the function $s_x = (S_x/f_x)^{1/2}$ with

$f_x = \Sigma_i m_i - l - 1$. The $S_0$ value should be smaller than the residual sum $S_\infty$. This corresponds to the hypothesis of parallel lines, to assure that the found common point of intersection is not an artefact due to the existence of isoenthalpic reaction series.

The existence of an IKR is usually accepted when the hypothesis 'there is a common point of intersection' cannot be rejected at a certain significance level, *i.e.* when $\bar{F}$ is smaller than the corresponding table value. This means (at a given significance level), that we cannot prove that there is no IKR. However, strictly speaking neither can it be proved that there is one. One has to accept that the large number of cases makes it more probable. For extremely accurate data the reversal hypothesis 'there is no common point of intersection' can be rejected by means of a comparison of a $\bar{F}' = 1/\bar{F}$ value with the corresponding $F$ table value $f_2$, and $f_1$ degrees of freedom. If the $\bar{F}'$ value is greater, one has to accept the existence of this IKR at the given significance level. As can be seen in Table I, such reaction series are already available.

## III. Experimental Examples for the IKR

Three series of first order reactions will be analysed exemplarily in detail in this section. For further experimental examples one might refer to refs. 1–5 and 11–25. The results of the statistical analysis carried out according to the methods given above are summarized in Table I. The reaction series have been chosen according to the following criteria: (a) the data should demonstrate a highly precise IKR (see Appendix); (b) elementary first order reactions are to be considered as they are compatible with the theoretical investigations [1, 2, 25]; and (c) information about the translation–vibration interaction and of the vibration–vibration interaction between reactant and surroundings should be accessible to allow a comparison with the theory [23–25].

### 1. The Thermal Dissociation of Diatomic Molecules

To give a proper example of an IKR the data for the thermal dissociation of diatomic gases highly diluted in argon [27–36] (which can be taken to be an inert gas) are presented in Fig. 1. This reaction series involves some points of interest which should be mentioned:

(i) This IKR is, compared to those commonly reported, extremely precise and is valid for a broad temperature range of approximately 15 000 K and a large number of measured data.

(ii) There exist also data for the dissociation of $Br_2$ and $F_2$. For studies involving $Br_2$ the IKR is less accurate, as these data are themselves much more scattered, but it can still be accepted at high significance. Including the $F_2$ data, however, would mean that the IKR must be rejected. However, if the IKR concept is worth investigating there must be of course an acceptable reason for excluding the $F_2$ data

TABLE I. Results of the Statistical Analyses of Common Points of Intersection of Arrhenius Plots

| Members of the reaction series | $T_{iso}$ (K) | $S_0(f_x)$ | $S_{00}(f_{00})$ | $S_\infty(f_\infty)$ | $\bar{F}(f_1, f_2)$ | $\ln k_{iso}$ | $E_a$ (kJ mol$^{-1}$) (unconstrained) | |
|---|---|---|---|---|---|---|---|---|
| Thermal dissociation of homonuclear diatomic molecules highly diluted in argon (see Fig. 1) | | | | | | | | |
| $Cl_2, D_2, H_2, J_2, N_2, O_2$ | 94339 | 22.55(259) | 22.44(255) | 361.7(260) | 0.243(5, 255) | 31.60 | 388.5 [a] | |
| $Br_2, Cl_2, D_2, H_2, J_2, N_2, O_2$ | 74074 | 24.48(314) | 23.80(309) | 363.47(315) | 1.534(6, 309) | 31.47 | 374.7 [b] | |
| $Br_2, Cl_2, D_2, F_2, H_2, J_2, N_2, O_2$ | 28985 | 41.43(334) | 36.31(328) | 569.12(335) | 6.92(7, 328) | 30.042 | 344.2 [c] | |
| Thermal decomposition of nitro-ethyl-benzoates (see Fig. 2) | | | | | | | | |
| Compound: **I to V** | 456.6 | 0.050(18) | 0.053(15) | 0.26(19) | 0.069(4, 15) | −4.67 | 91.96 [d] | |
| Compound: **I to VI** | 461.6 | 0.058(22) | 0.054(18) | 0.43(23) | 0.485(5, 18) | −4.43 | 94.16 [b] | |
| Isomerization of triphenylformazanes in toluene (see Figs. 3–8 and Table II) | | | | | | | | |
| Compound: **1, 2, 3, 4, 5** | 275.3 | 0.01(17) | 0.034(12) | 0.095(16) | 0.124(4, 12) | −4.84 | 73.86 [a] | process A |
| Compound: **6, 8, 9, 10** | 312.1 | 0.215(8) | 0.214(8) | 0.443(9) | 0.0074(3, 8) | −1.08 | 73.69 [d] | |
| Compound: **2, 3, 6, 8** | 273.2 | 0.059(6) | 0.058(6) | 0.122(7) | 0.0913(3, 4) | −12.27 | 41.32 [d] | process B |
| Compound: **7, 6, 9, 10** | 344.8 | 0.076(6) | 0.072(6) | 0.266(7) | 0.265(3, 4) | −7.86 | 64.95 [a] | |
| Compound: **1, 5, 7, 11** | 281.7 | 0.033(6) | 0.028(4) | 0.252(7) | 0.78(3, 4) | −13.09 | 30.15 [b] | |

[a] The $1/\bar{F}$ value $(f_2, f_1)$ is greater than the corresponding table value ($\alpha = 0.05$): the IKR has to be accepted at a significance level of 95%. [b] The $\bar{F}$ value $(f_1, f_2)$ is smaller than the corresponding table value ($\alpha = 0.01$): the IKR hypotheses cannot be rejected at a significance level of 99%. [c] The $\bar{F}$ value $(f_1, f_2)$ is greater than the corresponding table value ($\alpha = 0.01$): the IKR hypotheses has to be rejected at a significance level of 99%. [d] The $1/\bar{F}$ value $(f_2, f_1)$ is greater than the corresponding table value ($\alpha = 0.01$): the IKR has to be accepted at a significance level of 99%.

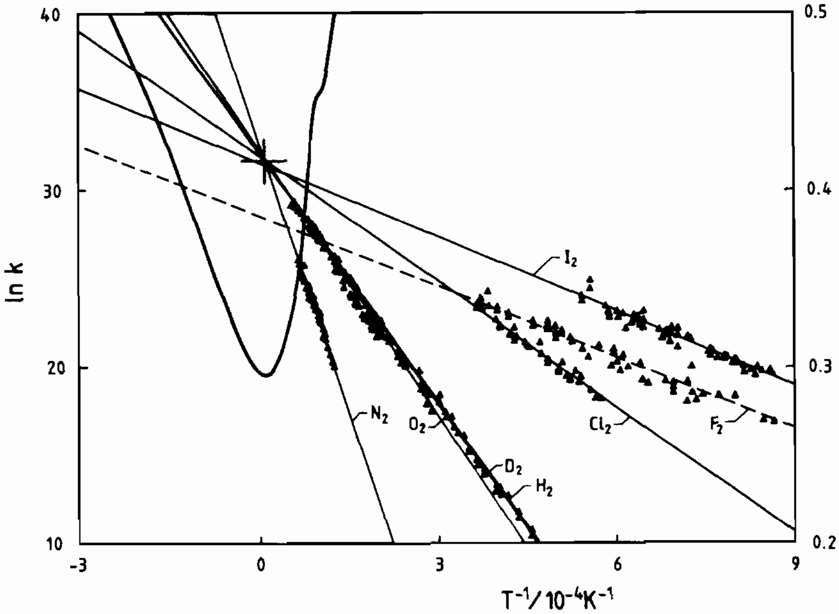


Fig. 1. Arrhenius plots for thermal dissociation of homonuclear diatomic gases highly diluted in argon. The curved line refers to the sum of squares of deviations of constrained straight lines from measurement points.

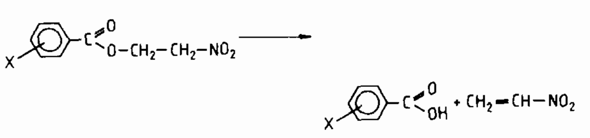
from the series. It may be pertinent therefore that $F_2$ has been found [33, 34] to react with argon at the given temperatures (which is not the case for the other gases).

(iii) It has been argued by some authors [37–41] that the compensation effect should not be expected to occur in gas phase reactions. The results presented here would seem to contradict this point of view.

(iv) The common point of intersection shifts to somewhat higher $1/T$ values as reactions with lower activation energies are involved.

### 2. *The Thermal Dissociation of Nitro-ethyl-benzoates*

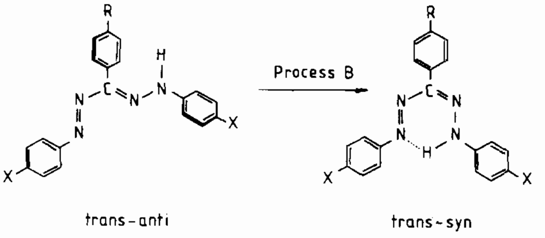
The reaction



with the substituents X: **I**, X = H; **II**, X = *p*-Cl; **III**, X = *p*-Br; **IV**, X = *m*-$NO_2$; **V**, X = *p*-$NO_2$; **VI**, X = 3,5-$NO_2$ has also been measured [42] in the gas phase without the presence of a diluting gas. The temperature range varies from 130 to 175 °C; the Arrhenius plots are given in Fig. 2. The $x_{iso}$ value (which again is highly precise when the disubstituted reactant VI is excluded; see Table I) is found to be much more positive ($x_{iso} = 1/RT_{iso} = 2.63 \times 10^{-4}$ mol $J^{-1}$) compared to the above gas phase reaction.

### 3. *The Isomerization of Triphenylformazanes*

This reaction involves two processes given by



Both processes have been studied in the liquid phase, using toluene as a solvent [43]. The substituents and their positions in the molecules are given in Table II.

Potentially there are two ways in which such an isomerization can take place; namely a rotation mechanism and an inversion mechanism. Sueishi and Nishimura [43] argued, by using the enthalpy–entropy proportionality as the criterium (see Fig. 3),

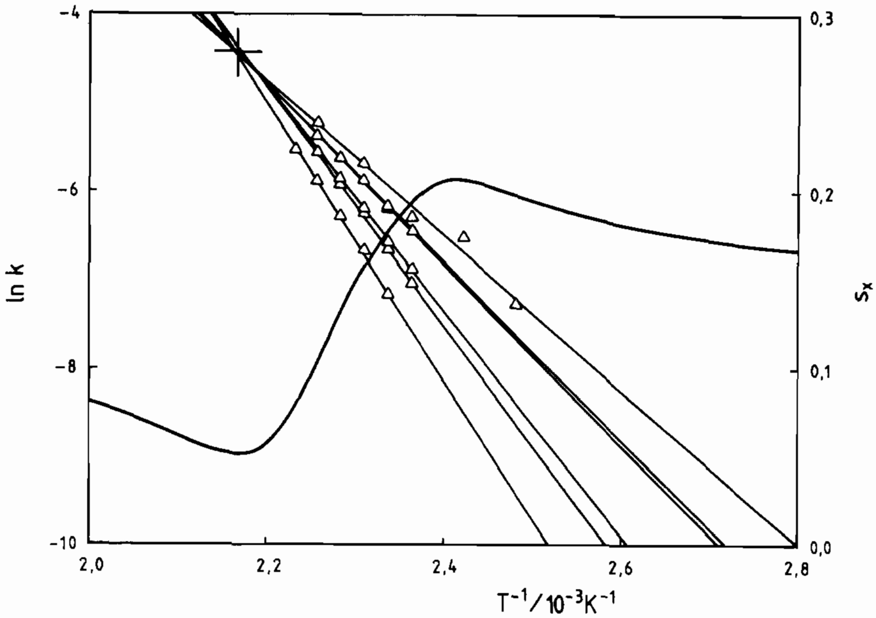
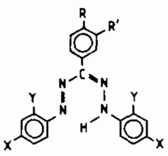


Fig. 2. Arrhenius plot for the thermal decomposition of nitroethyl-benzoates. The curved line refers to the sum of squares of deviations of constrained straight lines from measurement points.

TABLE II. Substituents of the Triphenylformazanes

| Structure | Compound | Substituents | | | |
|---|---|---|---|---|---|
| | | 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 |

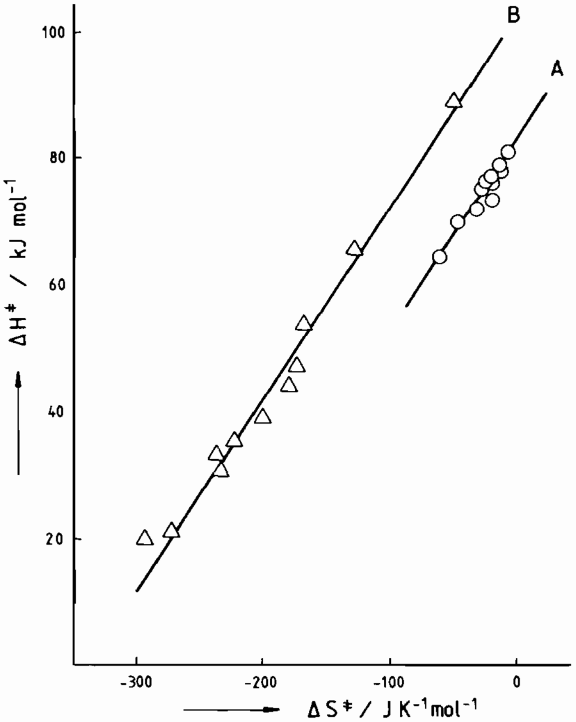


Fig. 3. $\Delta H^{\#}$:$\Delta S^{\#}$ plot for the thermal isomerization of triphenylformazanes in toluene: process A (○) and process B (△).

that there exists only one reaction mechanism, namely the inversion mechanism. However, Table I and Figs. 4–8 clearly demonstrate that a correct statistical analysis (described below) identifies at least two IKRs for each series. This fact has to be interpreted that there are at least two different reaction pathways present in both processes, dependent upon the substituent. For substituents strongly polarizing the $\pi$-electron system at the reaction site, the rotation mechanism accompanying the charge separation might be possible. Moreover it has been reported [44, 45] that the activation energies for the rotational isomerizations of guanidine salts around the C=N bond and some olefines around the C=C bond can be as low as 80 kJ $mol^{-1}$ (or even less). It seems to be meaningful to suggest that in the process A only the compounds **1**–**6** react via the inversion mechanism. The compounds **6**–**10** involve substituents which are able to act $\pi$-polarizing at the N=N site and can be

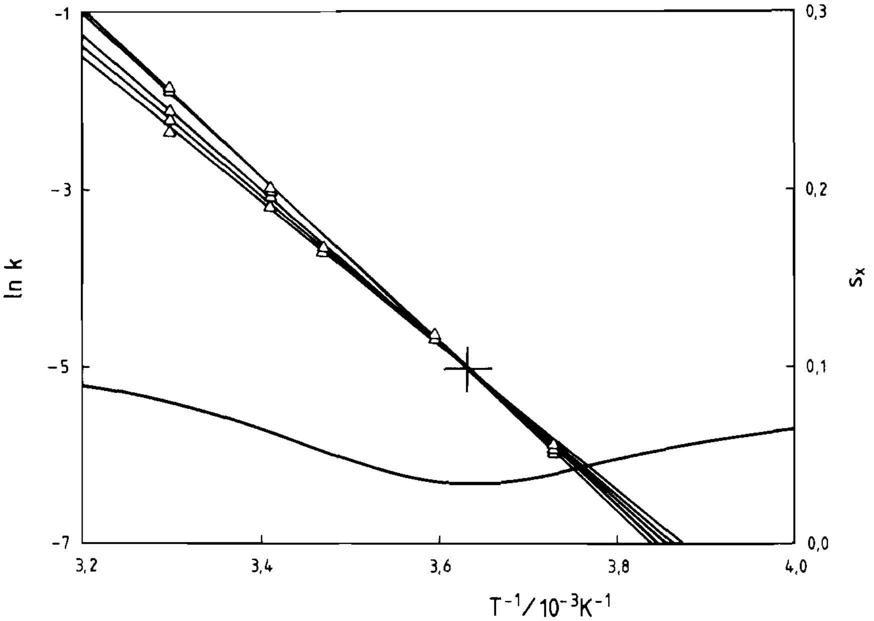


Fig. 4. Arrhenius plot for the thermal isomerization of triphenylformazanes in toluene: process A; compounds **1** to **5**. The curved line refers to the sum of squares of deviations of constrained straight lines from measurement points.

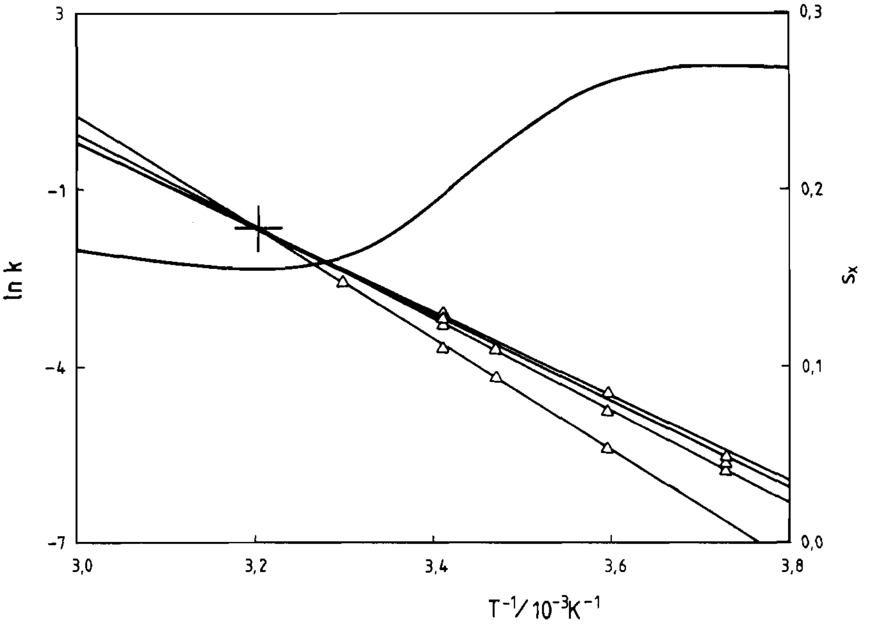


Fig. 5. Arrhenius plot for the thermal isomerization of triphenylformazanes in toluene: process A; compounds **6**, **8**, **9** and **10**. The curved line refers to the sum of squares of deviations of constrained straight lines from measurement points.

associated with the rotational mechanism. The former substituents exhibit an IKR with a $x_{\text{iso}}$ value of $4.37 \times 10^{-4}$ mol $J^{-1}$, and the latter corresponds to an IKR with $x_{\text{iso}} = 3.85 \times 10^{-4}$ mol $J^{-1}$. It can be seen from Figs. 4 and 5 that both IKRs are highly precise with the common points of intersection within or near the experimental temperature range.

For process B the compounds seems to fall into three groups (see Figs. 6–8). It should be mentioned, that due to the small number of experimental data and the narrow temperature range, the members of this groups may possibly change when more data would be available. However, the IKR involving the compounds 7–**10** seems to correspond with a $x_{\text{iso}}$

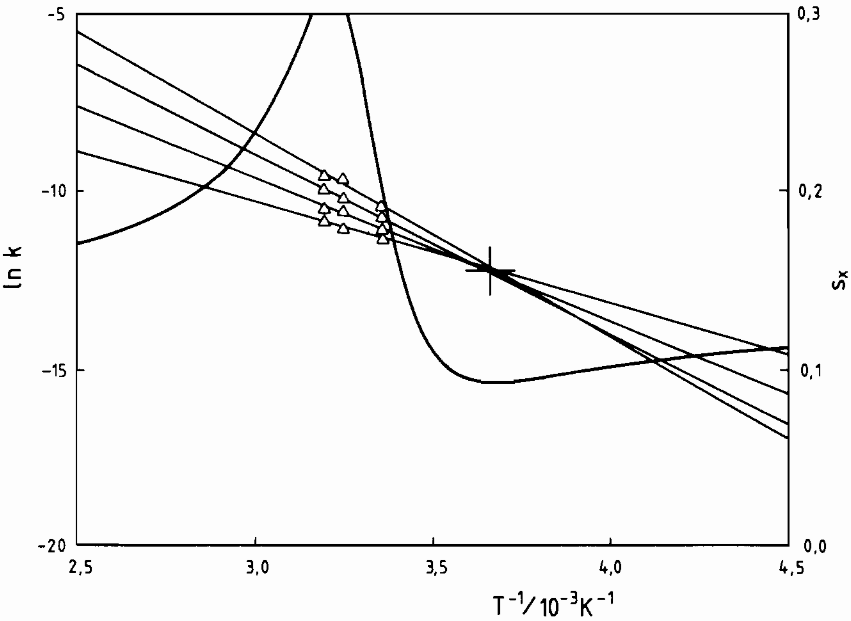


Fig. 6. Arrhenius plot for the thermal isomerization of triphenylformazanes in toluene, process B; compounds **2**, **3**, **6** and **8**. Curved line refers to sum of squares of deviations of constrained straight lines from measurement points.

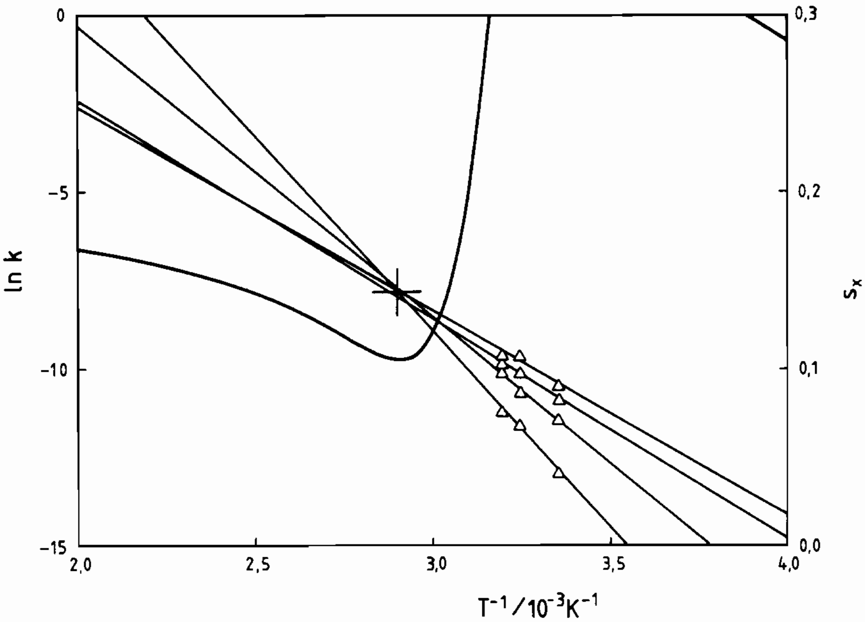


Fig. 7. Arrhenius plot for the thermal isomerization of triphenylformazanes in toluene, process B; compounds **7**, **8**, **9** and **10**. Curved line refers to sum of squares of deviations of constrained straight lines from measurement points.

value of $3.48 \times 10^{-4}$ mol $J^{-1}$ to the rotation mechanism in view of the substituents (now interacting with the C=N site). The $x_{iso}$ value is found to equal approximately the $x_{iso}$ value for the rotation mechanism at process A. The $x_{iso}$ values of the IKR of the compounds **2**, **3**, **6** and **8** ($x_{iso} = 4.40 \times 10^{-4}$ mol $J^{-1}$) and of the compounds **1**, **5**, **7** and **11** ($x_{iso} = 4.30 \times 10^{-4}$ mol $J^{-1}$) agree well with the $x_{iso}$ value of the inversion mechanism for process A. It is not clear, however, whether the distinction of the last two series is significant or only due to the narrow temperature range.

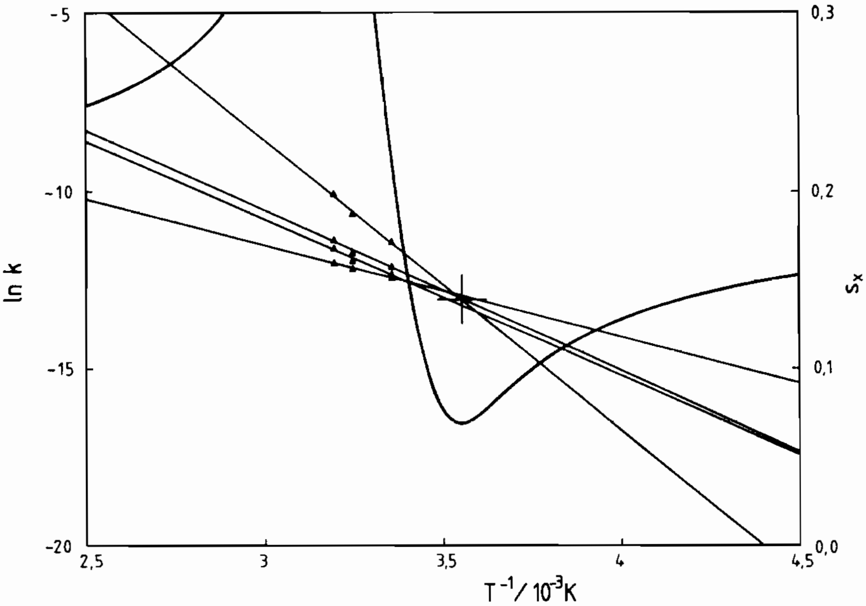


Fig. 8. Arrhenius plot for the thermal isomerization of triphenylformazanes in toluene, process B; compounds **1**, **5**, **7** and **11**. Curved line refers to sum of squares of deviations of constrained straight lines from measurement points.

## IV. Interpretation of the Physical Significance of the Isokinetic Temperature

In the first two papers of this series a statistical mechanical model for the IKR was presented [1, 2]. This model was based on the availability of the energy necessary to overcome the reaction barrier from some oscillatory degrees of freedom. For reaction series where significant changes in the activation energies appear (*i.e.* where the reaction rate is strongly dependent on the energy available in the system) the isokinetic temperature has been found as

$$T_{\text{iso}} = \bar{E}/R(s-1) \tag{6}$$

where $\bar{E}$ is the mean energy barrier and $s$ is the number of oscillatory degrees of freedom. Potentially two characteristic parameters may be extracted from this equation: (i) on estimating an energy barrier the number of oscillatory degrees of freedom involved in the activation process may be calculated and (ii) $T_{\text{iso}}$ should be related to a characteristic energy transition as expressed in a frequency of vibration of the system by

$$\nu = k_B T_{\text{iso}}/h \tag{7}$$

One perspective of this is to view the oscillations in a required heat bath where the energy necessary to overcome the barrier is stored.

The first reaction series considered above has been performed in the gas phase highly diluted with argon so that the activation of the reactants should be due only to collision with non-vibrating particles. From the mentioned theory [1, 2] one would expect an 'isoentropic' reaction series with the intersection point somewhat shifted towards more positive values with decreasing activation energies of the series. Using the mean unconstrained activation energies as an approximation for the energy barrier and assuming $(s-1) \approx 1$ for the diatomic oscillator the calculated $x_{\text{iso}}$ value for the series given above is $2.6 \times 10^{-6}$ mol $J^{-1}$. This is about twice the experimental value and may be accepted when knowing that the model has been based on an energy distribution to a larger number of oscillators. It may be interpreted however, such that some half of the diatomic oscillators are frozen. A calculation of a heat bath frequency is meaningless as the reaction is performed in an inert gas atmosphere (without vibrational degrees of freedom) and the reactants have no oscillatory degrees of freedom others than the reactive one.

At the thermal dissociation of the nitro-ethyl-benzoates the reciprocal isokinetic temperature $x_{\text{iso}}$ is shifted towards more positive values compared with the former reaction series. According to eqn. (6) $(s-1)$ is calculated as 24. This agrees well with the number of possible stretching vibrations of the reactants which is 23 to 25 according to the above substituents. (It is assumed that only such vibrations are active in the activation process of dissociation reactions.) An active heat bath frequency of 317.3 $cm^{-1}$ is calculated from the isokinetic temperature. A normal coordinate vibrational analysis (performed with the help of Prof. G. Bauer, Inst. of General Chem. TU, Vienna) of the nitro-ethyl-benzoate molecule, of which in this case constitutes the heat bath, shows 58 eigen-frequencies (Partly they have been fitted to experimentally known infra-red absorption bands of the molecule.) In the interesting region vibrations at the following wave numbers have been calculated: 244.1, 284.4, 332.9, 407.1 and 409.6 $cm^{-1}$. At 332.9 $cm^{-1}$ the atoms of the benzene ring perform an out-off plane vibration. In light of this accordance between the heat bath frequency and the frequency assigned from the present theory to the $x_{iso}$ position experimental far infrared data of the nitro-ethyl-benzoates would be highly desirable.

The value for $(s - 1)$ is found to be 32.5 and 28.4 for the two series in process A and between 12 and 22 for process B of the isomerization of the triphenylformazanes. The number possible of stretching vibrations of the reactants are about 40. As this reaction is performed in condensed phase, the solvent should act as the heat bath rather than the isolated molecule. This is seen from the active heat-bath frequencies calculated according to eqn. (8) between 190 and 240 $cm^{-1}$. Using the $x_{iso}$ value of the compounds **6**, **8**, **9** and **10** for process A which should be most accurate one according to the $F$ parameter, a $\nu$ value of 217 $cm^{-1}$ is calculated. The far infra red spectrum of toluene is shown in Fig. 9 (measured at the Inst. of Anal. Chem. of the TU Vienna with toluene p.A. (Merck/Darmstadt) using a 0.1 mm CsJ cell. The bands at 418 $cm^{-1}$ correspond to a water content of less than 0.03%). In agreement with the above calculated value the spectrum shows an absorption band at 218 $cm^{-1}$.

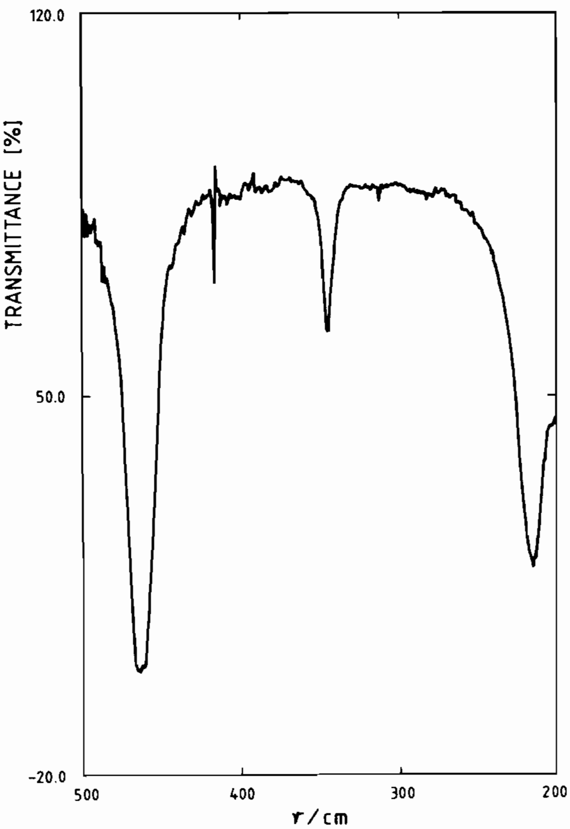


Fig. 9. Far infra-red spectra of toluene measured in a 0.1 mm CsJ cell.

## V. Discussion

On the basis of both experimental data and theory [1–4, 23–25] it can be argued that the IKR is a real phenomenon and is of physical significance. The occurrence of an invariant point in the Arrhenius plot at an isokinetic temperature corresponds to an interaction between the reactants and the available heat bath. The heat bath–reactant interaction may be taken as being equal (or invariant) with respect to all members of a considered reaction series. The position of $x_{iso} = 1/T_{iso}$ might be used to characterize chemical reaction series as it is related to the availability of energy in the series. The argument that the frequency calculated from the isokinetic temperature is an active heatbath frequency is supported also by bimolecular [24] reaction series as well as by thermodynamic data [25]. Due to the close connection between the isokinetic temperature and vibrations of the reaction heat bath, far infrared studies may bring much more information to our knowledge of reactions performed in condensed phase than commonly thought.

Negative $x_{iso}$ values have been observed [4–6] and may be explained in terms of kinetic processes that can be separated into two steps, those more strongly affected by the overall energy and those affected by the overall entropy, with both steps oppositely controlled by substituents [3, 4]. This was, however, the reason for choosing examples which may be treated as elementary reactions. However, $x_{iso}$ values may be dissected into those which are below or above the experimental temperature range. The third reaction series given above (*i.e.* the isomerization reaction of the formazanes) illustrates both cases. In the former case the selectivity within the reaction series is decreased with increasing temperature whereas in the latter the selectivity is increased. This would mean that the active heat bath frequencies are higher in energy than $kT$ for the experimental region in the former case, whereas they are lower in the second one. At the isokinetic temperature a minimum in selectivity within the reaction series is due to a maximum in energy transfer from heat bath to reactant. Further and more detailed investigations will relate the results of the present paper to a more general theory [23–25].

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