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## A RESULT OF RESONANT ENERGY EXCHANGE BETWEEN REACTANTS AND THEIR CHEMICAL SURROUNDING: THE ISOKINETIC RELATIONSHIP

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Many homologous series of reactions exhibit a common point of intersection in the  $\ln k$  versus  $1/T$  plots. This can be taken as a profound basis for the appearance of the isokinetic relationship (IKR) defining a temperature where rate (or equilibrium) constants of the series show a minimum in selectivity. The theoretically derived relationship describing the IKR and yielding a correlation between the isokinetic temperature and the frequencies available in an ideal heat bath is examined for real systems. It is shown that the role of the solvent in chemical reactions that exhibit isokinetic relationship is not only due to chemical interactions but also to energy transfer between reactants and solvents and vice versa.

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Nearly sixty years ago the idea of the "compensation effect"<sup>1-14</sup> was born when Constable<sup>1</sup> compared the activation energies ( $E_a$ ) and the logarithm of Arrhenius pre-exponential factors of the dehydrogenation of alcohol measured at a series of different prepared copper-oxide catalysts. Since this a great many of investigations of this effect appeared, leading to a lot of controversies and misunderstandings.

Assuming that we have in analogy to Constables work values of rate constants ( $k_i$ ), pre-exponential factors ( $A_i$ ), and activation energies ( $E_{a,i}$ ) for a series of closely related reactions (denoted by an index  $i$ ). Using Arrhenius equation they may be related by

$$k_i = A_i \exp(-E_{a,i}/RT). \quad (1)$$

From this the main reason for the all to common dismissal<sup>15-17</sup> of the compensation effect, (which is defined as a proportionality of enthalpic and entropic terms of rate or equilibrium constants for a series of similar reactions) can be seen, when it is realized that it is not possible to perform a linear regression analysis on statistically interdependent variables<sup>18-22</sup>. Enthalpies and entropies resulting from the slopes and intercepts of Arrhenius- or van't Hoff plots are such statistically interdependent values and therefore all arguments, either accepting or rejecting the existence of this effect,

are misleading as long as they are based on these derived values. It has been shown that there is a possible way out of this quandary, namely by using the original data (i.e. the rate of equilibrium constants measured at different temperatures) to prove the existence of a common point of intersection of the Arrhenius of van't Hoff plots<sup>19-21</sup>.

Rewriting the linear relationship between  $E_a$  and  $\ln A$

$$\ln A_i = \ln k_{\text{iso}} + E_{a,i}/RT_{\text{iso}} \quad (2)$$

with Eq. (1) we get,

$$k_i = k_{\text{iso}} \exp(-E_{a,i}(1/RT - 1/RT_{\text{iso}})) \quad (3)$$

which gives in the  $\ln k$  versus  $1/T$  plane (namely the Arrhenius plane) a family of straight lines intersecting at an ordinate position of  $\ln(k_{\text{iso}})$

$$\ln(k_i) = \ln(k_{\text{iso}}) - E_{a,i}(1/RT - 1/RT_{\text{iso}}) \quad (4)$$

and an abscissa value of  $1/T_{\text{iso}}$ . It has been Exner<sup>18,19</sup> who suggested that this single point of intersection of the Arrhenius lines can be used for a sound statistical test

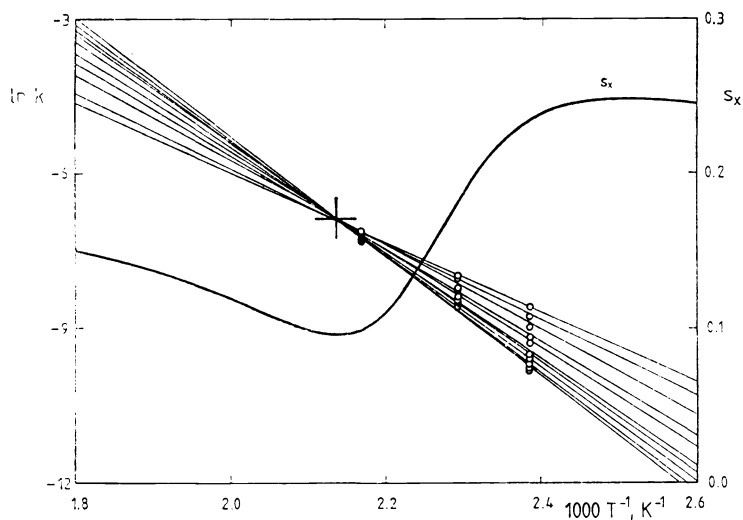


FIG. 1

Arrhenius plots of the formation of anilides of N-phenyl-sarcosine<sup>23</sup> from dimethylaniline with substituted chloroacetanilides in octanol. (Substituents in sequence of decreasing rate constant at the mean experimental temperature: *p*-NO<sub>2</sub>, *p*-CH<sub>3</sub>CO, *m*-NO<sub>2</sub>, *m*-I, *p*-Br, H, *m*-Br, *m*-CH<sub>3</sub>, *p*-CH<sub>3</sub>, 3,4-(CH<sub>3</sub>)<sub>2</sub>, *p*-O-CH<sub>3</sub>;  $T_{\text{iso}} = 467$  K;  $\ln k_{\text{iso}} = -6.9$ )

since  $\ln k$  and  $T$  are statistically independent, and this is the basis of the *Isokinetic Relationship* or IKR. Sound statistical procedures has been derived, are available<sup>21</sup> and should be a necessary tool to each scientist working in the field of temperature dependent rate or equilibrium constants. A good example of a statistically sound IKR is the reaction of dimethylaniline with substituted chloroacetanilides<sup>23</sup> (see Fig. 1). The information contained in such plots, (which can be in either the Arrhenius or van't Hoff planes) exhibiting a common point of intersection, lies at the center of the IKR.

Both of these effects, namely the compensation effect and the IKR, can of course be expressed in differential form: Using Leffler's operator<sup>5</sup>,  $\delta$ , ( $\delta$  refers to the variation of discrete values within the considered series) we have, for a single interaction mechanism, a linear plot of  $\ln(A_i)$  versus  $E_{a,i}$  with a slope given by

$$\delta \ln A / \delta E_a = 1/T_{iso} \quad (5)$$

and Eq. (6) can be used as a definition of to the compensation effect.

In the same way, by using a *continuous* parameter ( $\xi$ ) instead of the discrete  $i$ -values we may write the IKR as

$$\left. \frac{\partial \ln k(\xi)}{\partial \xi} \right|_{1/T_{iso}} = 0 \quad (6)$$

meaning that a temperature exists where differences between  $\ln k$  within the series show a minimum<sup>24-26</sup>, i.e. there is a minimum in *selectivity* (see also Giese<sup>27,28</sup>). The representation Eq. (7), which is the most general of all, will be used in this work whenever the physical background of the IKR is considered. However, for simple discussions, we may still use the proportionality given in Eq. (5) or the straight-forwards graphical representation of the common point of intersection like the example given in Fig. 1.

From a collection of a large number of IKR's exhibiting high statistical significance it can be concluded that the IKR is not an artefact<sup>25,26,29</sup>. This fact obviously leads to the necessity of a theoretical description to this effect and to the question of the physical meaning of the characteristic parameters especially of  $T_{iso}$  (refs<sup>25,26</sup>).

## RESULTS

### *Theoretical Description of the Isokinetic Relationship*

In Kramers theory<sup>30</sup> of rate constants reactant molecules are supposed to become activated through their collision with other molecules of the surrounding medium, which act as a constant-temperature "heat-bath". After a random-walk over discrete

energy levels of the reactants, they reach, at the highest point of the barrier, a point of no return. The crossing over this barrier constitutes the chemical reaction rate. Kramer's representation of a Markoff process can be rewritten in the form of a Langevine equation<sup>26</sup>:

$$\frac{\partial \sigma(t)}{\partial t} = \frac{\partial}{\partial l} R(l) \left[ \frac{\partial \sigma}{\partial l} + \frac{1}{k_B T} \hbar \frac{\partial}{\partial l} \omega(l) \sigma \right] + g(l). \quad (7)$$

In this  $\sigma$  represents the time dependent density of reactant-particles in the energy level  $l$ .  $R(l)$  represents the quantum-mechanical transition probability from a level  $(l-1)$  to  $l$  which is governed by the form of energy exchange between reactants and their molecular surrounding.  $\omega(l)$  represents the energy of the level  $l$  in form of a frequency and  $g(l)$  provides a source term to allow for a steady state solution of the differential equation. The variables  $k_B$ ,  $T$ ,  $\hbar$  and  $t$  have their usual meaning. Defining further a net flux  $\Phi$  of reactant particles over the barrier (represented by  $l_{\max}$ )

$$\Phi(l_{\max}) = \int_0^{l_{\max}} g(l) dl = -R(l) \left[ \frac{\partial \sigma}{\partial l} + \frac{1}{k_B T} \hbar \omega(l) \sigma \right] \quad (8)$$

and a reactant concentration  $x_R$

$$x_R = \int_0^{l_{\max}} \sigma(l) dl \quad (9)$$

we can define a first order rate constant  $k$  by

$$k = \Phi(l_{\max})/x_R. \quad (10)$$

Under the condition of large barriers a steady-state solution has been obtained for a the above sets of equations describing a non-equilibrium distribution of reactant molecules among discrete energy levels, with a point of no return at an energy barrier, and connected with a surrounding heat-bath. It has been assumed that during a reaction a non-equilibrium steady-state distribution of reactant particles is present so that the solution of the differential equation (7) takes the form<sup>26,31</sup>:

$$k = \Phi(s_N) \left\{ \int_0^{s_N} dl \exp \left( - \frac{\hbar}{RT} \int_0^l \omega(l'') dl'' \right) \int_0^{s_N} dl' \frac{\exp(1/RT) \int_0^{s_N} \omega(l'') dl''}{P(l')} \Phi(l') \right\}^{-1}. \quad (11)$$

This integral may be solved by partial integration and thereupon yields, assuming that the energy barrier is much larger than  $k_B T$ , the following simple form:

$$k = A_0(\hbar\omega/k_B T) P_{s_N, s_N-1} \exp(-s_N \hbar\omega/k_B T). \quad (12)$$

The terms  $A_0$ ,  $s_N \hbar \omega$ ,  $T$  and  $P_{s_N, s_{N-1}}$  represent a constant involving mainly the collision number, the energy barrier height, and the temperature of the molecular surroundings of the reactants (i.e. the heat-bath) and the quantum-mechanical transition-probability of a transition between the reactant level  $s_{N-1}$  to the highest reactant level (i.e. the point of no return)  $s_N$ , respectively. This approach provides a key to the understanding of the IKR (ref.<sup>26</sup>).

The problem of understanding the IKR is at this point transferred to the problem of the quantum-mechanical transition probabilities  $P_{s_N, s_{N-1}}$  (ref.<sup>26</sup>). In condensed phases it must be assumed that the heat-bath also contains energy stored in the form of vibrational degrees of freedom. The appropriate transition probabilities can be calculated<sup>26</sup> and yield for vibration-vibration interactions to:

$$P_{1,m} = l \exp(\omega/\nu). \quad (13)$$

In this a resonance condition of the form

$$\nu m = \omega l \quad (14)$$

is included meaning that energy is exchanged with the highest probability at equal energies. ( $m$  represents the number of the heat-bath level,  $\nu$  the associated frequency, and the resonance condition is given in its form for harmonic oscillators.) Using this, the following form of the rate constant is found

$$k = A_0 s_N (\hbar \omega / k_B T_{\text{exp}})^2 \exp[-s_N(\omega/\nu - \hbar \omega / k_B T_{\text{exp}})]. \quad (15)$$

Here  $\nu$  represents a vibrational heat-bath frequency predominantly active in the energy exchange with the reactants. From this the IKR follows naturally. When, for example, considering the reactants, the frequency  $\omega$  associated with a vibration along the reaction coordinate can be identified with  $\xi$  from Eq. (6)

$$[\partial \ln k(\omega) / \partial \omega]_{T_{\text{iso}}} = 0. \quad (16)$$

Applying this condition to Eq. (15) a relation is found between  $T_{\text{iso}}$  and the vibrational frequency predominantly exchanging energy with the reactants present in their molecular surroundings:

$$1/RT_{\text{iso}} = 1/E + 1/N_L \hbar \nu \quad (17)$$

(where  $h$  Planck's constant;  $N_L$  Avogadro's number;  $k_B$  Boltzmann's constant;  $\nu$  the predominantly active heat-bath frequency). The first right-hand term is associated with collision activation and may be neglected for reaction series where

vibrational activation is possible. In this case

$$1/RT_{\text{iso}} = 1/N_L h\nu \quad (18)$$

should be valid. It should be pointed out at this point that  $\xi$  may also be identified with the maximal number of reactant energy levels  $s_N$  yielding the same result. This means that, in whatever form the members of the series are represented, they exhibit the same rate at  $T_{\text{iso}}$  or show a minimum in selectivity at this temperature.

It is significant for this approximation that in the gas phase, where the energy exchange is by individual collisions, the experimental results show  $1/T_{\text{iso}}$  values near zero, i.e. isentropic behavior is observed. At  $T_{\text{iso}}$  the dependence upon  $\xi$  vanishes from the rate equations and the members of the reaction series cannot therefore be identified by means of their rate constants, i.e. they exhibit *isoselective behavior*.

No group-theoretical selection rules have been explicitly built into the model as the heat-bath was assumed to be structureless only containing vibrational frequencies. However, in some sense, because the reacting species have a real chemical identity, selection rules have been implicitly invoked, i.e. because most chemical reactions involve a change in polarity rather than in polarizability, IR-active vibrations — as opposed to Raman active ones — are more likely to excite the reacting species.

#### *Experimental Tests for the Theory*

A general outcome of the theory is that the Boltzmann energy of  $T_{\text{iso}}$  should exist as a frequency in the vibrational spectrum of the heat-bath i.e. of the solvent or catalyst. Or, reversing the argument, for a given solvent an isokinetic temperature may only be found within discrete regions corresponding to the absorption bands of the vibrational spectrum of the solvent. Examples illustrating this are displayed in Fig. 2. They show the range of frequencies corresponding to the range of experimentally found  $T_{\text{iso}}$  superimposed on the IR-spectra of the solvents concerned. This has been confirmed by examination of some 150 reaction series<sup>25,29</sup>, all established by means of a proper statistical analysis, and chosen under the condition that *a*) they are statistically highly significant IKR's and *b*) their  $T_{\text{iso}}$  value is within  $\pm 5\%$  (even when extrapolated). The data may be divided into three groups according to (i) IKR's in homogeneous reactions with a variation in the reactants; (ii) IKR's in solutions when solvents are varied (i.e. isosolvent relationships) and (iii) IKR's found in heterogeneous catalysis.

The data for several homogeneous<sup>25</sup> and heterogeneous<sup>29</sup> reaction series performed in different solvents or on different solid catalysts are summarized graphically in Fig. 3 and in Fig. 4, respectively. Although the broadness of some absorption bands makes a coincidence of theory and practice inevitable in these cases, the other systems show a relatively strict accordance with theory.

Experimentally found isokinetic temperatures  $T_{\text{iso}}$  of various chemical reaction series vs the absorption bands observed in the infrared spectra of the solvents.

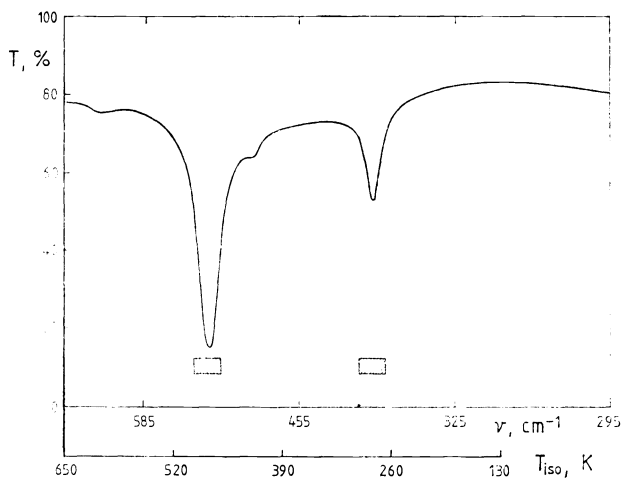


FIG. 2

Far infrared spectrum of acetone and the range of  $T_{\text{iso}}$  values found at various reaction series performed in this solvent

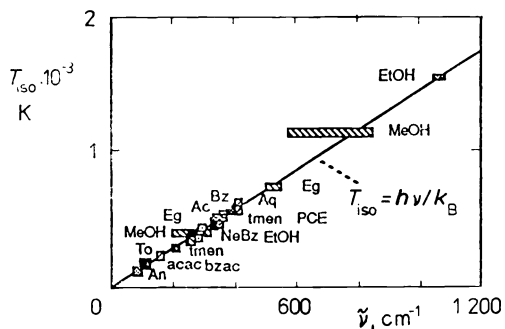


FIG. 3

Isokinetic temperatures of various reaction series measured in different solvents versus the corresponding IR-absorption bands of the solvent<sup>25</sup>

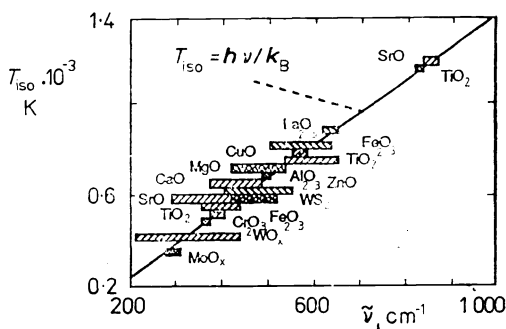


FIG. 4

Isokinetic temperatures of various heterogeneous reaction series and corresponding solid catalysts (catalysts are represented by simplified formulas because they are often non-stoichiometric<sup>29</sup>)

Figure 3 particularly clearly indicates a linearity between  $T_{iso}$  and an observed IR-frequency as required by Eq. (24) and this relationship will be examined in more detail below. The data pertinent to heterogeneous catalysis (Fig. 4) is, as might well be expected, less convincing because more of the IR-bands are of necessity generally very broad in the required region. This explains that in contrary to homogeneous systems, where isosolvent relationships are rare because of the condition of overlapping frequencies of all solvents of the series, IKR's with a catalyst variation i.e. a variation of the heat bath, may be found. In fact, many scientists working in heterogeneous catalysis associate with the term compensation effect or IKR merely a catalyst variation than a reactant variation. The necessity of a careful statistical analysis of experimental data should be pronounced especially for heterogeneous systems because a great many of publications exist in this field where activation energies are plotted versus activation entropies yielding artefacts. Nevertheless, a general correlation is evident.

A major problem requiring examination remains, however, – namely to examine to what extent it is possible to predict which band in the infra-red spectrum of the solvent is the “active” one. Note that to date no frequency calculated from a  $T_{iso}$  value lies in an IR window of the solvent concerned.

It should also be possible to show that the IKR *breaks down or moves to another  $T_{iso}$  when the active frequency is removed*. This is of crucial importance to the theory. Consider the case where an IKR reaction is performed in solvent mixtures with  $T_{iso}$  related, as long as one solvent is in excess, to a frequency corresponding to an IR-band of this solvent, but at the same time corresponding to an IR-window of the other solvent. This is the case at the following two examples: The IKR breaks down completely at complex formation between nickel(II) and 2,2'-bipyridyl in water-methanol mixtures<sup>32</sup> when methanol is added up to large excess. The same reaction, performed in acetonitrile-methanol mixtures<sup>33</sup> yields a new IKR a new  $T_{iso}$  corresponding to a new frequency, now available in methanol. Another example of a reaction system exhibiting this effect is the solvolysis of tert-butylchloride in solvent mixtures<sup>34,35</sup>.

A variation of the heat-bath itself (i.e. solvent variation) may also yield isokinetic relationships but under the *strong restriction that the all solvents of the series have the same active vibrational frequency*. It is obviously not often the case that for a collection of solvents the necessary frequencies overlap. The reduction potentials of four different quinones have been measured in five different solvents. It was found that different quinones did not show isokinetic (iseo-equilibrium) behavior: they are obviously different in more than one parameter and do not fall into one series. However a *solvent variation* yielded for each of the quinones highly significant common points of intersection. The isokinetic temperatures are found to be almost the same for the different quinone series and correspond to available IR-frequencies of the solvents. The plot for only one of the solvents (namely that for acetonitrile)



does not meet the common point of intersection and it is significant that this solvent has no absorption frequency in the appropriate region. Similar situations are found for isosolvent relationships for the electro-reduction of some solvatochromic nickel(II) (ref.<sup>37</sup>) – and copper(II)-complexes<sup>38</sup>; imine-enamine tautomerism<sup>39</sup>; chlorine isotopic exchange reaction; and olefine cycloaddition<sup>40</sup> as given in reference<sup>26</sup>.

All these observations of IR absorption bands being linked in some way to  $T_{\text{iso}}$  through an IKR may be taken as a hint that a resonance condition determines the “chosen” IR-frequency corresponding to an isokinetic relationship. The fact that in the study of the electro-reduction of quinones in various solvents (above) the reactants themselves exhibit IR-absorption at these frequencies might reinforce this conclusion.

Several authors, for example Leffler<sup>5</sup> and Grunwald<sup>6</sup> suggested that from the appearance of an IKR it can be concluded that only one reaction mechanism is present. The present theoretical description supports this as no general changes in the reaction profile (for example by including a new minimum or maximum according to an intermediate or a new barrier) are allowed for. In fact the IKR analysis has brought to light several, sometimes unexpected, examples of a change in mechanism:

The gas-phase dissociation of diatomic molecules such as  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{F}_2$  shows an excellent IKR (based on an enormous experimental temperature range)<sup>21,25</sup>. The series is isoentropic and in fact is coincidentally a good example for the isoentropic behavior of gas-phase reactions.  $\text{F}_2$  does not meet the intersection point and because the reactions were performed with argon as diluting gas this may be explained in terms of a reaction between  $\text{F}_2$  and Ar which indeed takes place over this temperature range – in contradistinction to all other members of the series.

Another example is given by the partitioning of pyridylalkylamides in octanol/water and dibutylether/water systems<sup>41,42</sup>. The partition coefficients of a series of 12 isomeric and homologous pyridylalkylamides split, rather surprisingly perhaps, into two groups when analyzed for an IKR. This can be explained by noting that one group is able to form intramolecular  $\text{N}\cdots\text{H}-\text{N}$  bonds while the other, on steric grounds, is not.

A third example is given with the isomerization of formazanes where with two IKR's two pathways according to a rotational and an inversional mechanism are found<sup>21,26,43</sup>. This example is of particular importance because the authors originally found only one straight line on the basis of a  $\Delta G$  versus  $\Delta S$  plot and argued that – contrary to their chemical expectations – only one reaction mechanism is present in this series. A statistically sound IKR-analysis<sup>21</sup> later clearly demonstrated the existence of *two* intersection points for this series of reactions. In other words two mechanisms are indeed present – in agreement with chemical intuition!

## CONCLUSIONS

We conclude from all the evidence so far collected that for a given solvent an isokinetic temperature may only be found within discrete regions corresponding to the absorption bands of the vibrational spectrum of the solvent. The rules to predict this region for a given reacting system are however unknown. What is perhaps most important, however, is the inescapable conclusion to be drawn from the theory that an isokinetic relationship is a natural outcome of an interplay between solvent and system and *ought to be expected* unless solvent molecules have a specific part to play in the reaction.

It is therefore obvious that further experimental results on both, the IKR itself and the measurement and interpretation of far IR-spectra are necessary to further prove the given relationship. Either way the results would be of vital importance in elucidating both the nature of this isokinetic effect and the role played by the solvent.

It should be mentioned that a close functional interrelation between the IKR and linear free energy relationships (LFER's) exist, which provides the possibility of predictions of both temperature and reactant (for example substituent) dependence<sup>44</sup>.

Several points are open to further investigation and may yield a large field of exciting scientific work in the future. There is, for example, the problem of predicting the change in the isokinetic relationship when the solvent is changed. To gain more information about this question far IR-spectroscopy performed on the heat-bath (i.e. solvents, catalysts) and the reactants is necessary. Both theoretical and practical work in this field is continued in our institute.

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