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On the isokinetic effect of ligand substitution reactions of $Ni(DMSO)_6^{2+}$ in DMSO solution

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Abstract

A model of selective energy transfer, originally developed for catalysis, is applied to explain the isokinetic temperature found for some substitution (and exchange) reactions of the hexasolvated complex of Ni(II) in dimethyl sulfoxide solutions. An analysis of the stepwise change of activation energies for these and similar reactions indicates that the threefold degenerate Ni–O stretching vibration is involved in the activation process. The reaction coordinate can be described as an expansion of one face of the octahedron, where the reactant enters, and the corresponding contraction of the opposite face.

Introduction

The isokinetic effect is defined by the intersection of the Arrhenius lines (ln k versus $1/T$) at one and the same point for a series of very closely related reactions. The point of intersection defines the isokinetic temperature, θ, and the phenomenon is often referred to as the compensation effect [1]. Often such series of closely related reactions are found in the field of catalysis where many different explanations have been offered [2]. Some years ago the present author suggested [3–5] that the isokinetic effect can be explained in terms of the selective transfer of energy from a suitable energy reservoir having the vibration frequency ω into that vibration mode of the reactant that best corresponds to the distortion of the molecule towards its structure in the activated state.

It was shown that it is possible to calculate the isokinetic temperature for any value of the frequency ω if one knows the value of the frequency, ν, of the vibration mode of the reactant. As in the description of vibrational spectra [6], the deduction relied on classical mechanics supplemented by the quantum character of energy changes. The resulting expression is

$$\theta = Nhc\ R\text{-}1\ (\nu^2\text{-}\omega^2)\omega^{-1}\{\pm\pi/2\text{-}arctg(0.5\nu\omega(\nu^2\text{-}\omega^2)^{-1}\}^{-1} \tag{1}$$

The basic idea behind this model is that the energy dissipation from excited levels of the reactant must be effectively counteracted by the transfer of energy in the way described above. If ω is very close to ν a state of resonance energy transfer is operating. For the perfect resonance condition $\nu=\omega$, eqn. (1) simplifies to

$$\theta = Nhc/2R\ \nu = 0.715\ \nu \tag{2}$$

In order to exemplify, perhaps verify, these relations one should like to use as accurate kinetic data as possible for as well defined systems as possible. In catalysis it is not always easy to define the system accurately as there are many operating factors, between which the relations are not always known. However, it is important to note that the energy dissipation implied in the model occurs for any reaction in a condensed phase. The consequence of this is that one might look for homogeneous reactions in solution of, for example, organic chemistry or coordination chemistry in order to get high precision data. Investigations of these fields of chemistry are often performed with the major aim of producing extremely accurate data. Having achieved such a verification one can trustfully apply the model to the much more complex and therefore much more difficult cases in heterogeneous catalysis.

Application

One such example will be dealt with in this paper, viz. ligand substitution reactions of the $Ni(DMSO)_6^{2+}$ ion in DMSO solution (DMSO = dimethyl sulfoxide).

$$Ni(DMSO)_6^{2+} + L = Ni(DMSO)_5L^{2+} + DMSO \tag{3}$$

Chattopadhyay and Coetzee [7] found that reaction (3), with L = pyridine, 1,10-phenanthroline, 2,2′-bipyridine and 2,2′,2″-terpyridine, yielded a perfect ex-

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ample of the isokinetic effect. The isokinetic temperature was found to be 393 K [7].

The reaction is commonly believed to be of the I_d mechanism with a dissociation of a Ni–O bond to set free one DMSO (oxygen bonded) at the same time as the other ligand is entering from the other side [8]. It is therefore the most reasonable assumption, within the model to be tested, that the vibration mode that will effect the transformation will be the (asymmetric) M–O stretching mode. The following paragraph will show the consequences of this assumption.

Spectroscopic data

The vibrational spectra of the $Ni(DMSO)_6^{2+}$ system has been well characterized [9–11]. Some pertinent data are reproduced in Table 1. In particular, the investigation of Berney and Weber [9a] is of great value. It shows that the IR active M–O stretching mode (the asymmetric one, threefold degenerate) appears at 444 cm^{-1}. If we use this figure in eqn. (1) the relation depicted in Fig. 1 results. From this Figure we can immediately note that the isokinetic temperature $\theta = 393$ K corresponds to either $\omega = 355$ or 560 cm^{-1}. It is obvious from the tables of Berney and Weber [9a] (reproduced in part in Table 1) that there are no corresponding modes in the free solvent, the most abundant heat bath system. However, there is a precise agreement with the δ'_{CSO} mode of the $Ni(DMSO)_6^{2+}$ complex itself, which is 350 cm^{-1}. ($\omega = 350$ cm^{-1} gives exactly $Q = 393$ K if one allows a slight variation of the M–O vibration to $\nu_{MO} = 440$ cm^{-1}. On the other hand Griffiths and Thornton [10] report 354 cm^{-1} for δ'_{CSO} which agrees as well with $\nu_{MO} = 444$ cm^{-1} to give the experimental value of the isokinetic temperature.)

TABLE 1. Vibrational data (cm^{-1}) of DMSO and $Ni(DMSO)_6^{2+}$ in the low wave number range

	$Ni(DMSO)_6^{2+}$	DMSO
M–O stretch	444 [9a], 443 [10]	
Sym. CSO deform., δ'_{CSO}	350 [9a], 354 [10]	384 [9a]
Antisym. CSO deform., δ''_{CSO}	321 [9a], 334 [10]	334 [9a]
C–S stretch	717, 684 [10]	690, 661 [9b]

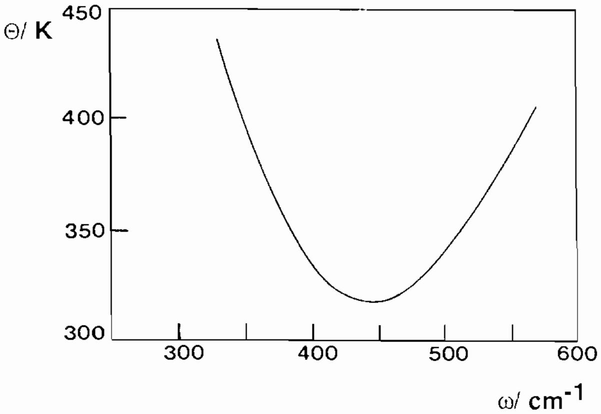

Fig. 1. Graphical representation of the function $\theta = \theta(\omega)$ according to eqn. (1) for the specific value of $\nu = 444$ cm^{-1}.

It thus appears that the isokinetic temperature 393 K arises from the availability of a well defined heat source within the complex. These vibrators are in thermal equilibrium and can extract energy by 'almost resonance' from the corresponding δ'_{CSO} mode (384 cm^{-1}) of the free solvent.

Activation enthalpies

It has been found empirically [4, 22], but it follows as a consequence of the model of selective energy transfer, that for closely related reactions there is a stepwise change of the activation energy or activation enthalpy. The increment has been found [4] to be multiples of the vibration quantum that characterizes the vibration ν mentioned above. It is therefore tempting to collect as many data of activation enthalpies as possible for substitution reactions involving $Ni(DMSO)_6^{2+}$. In Table 2 such a collation is presented taken from literature during the last two decades. Only reactions with neutral ligands L have been selected. The original data expressed in kcal mol^{-1} are presented as well, in order to indicate the original level of accuracy. Some data that do not have a very high precision have been discarded. From these data we have followed the procedure outlined in previous investigations of this kind [4, 23]. We sort together all data of approximately the same values and form the mean of these data assuming that all the data of similar magnitude represent one and the same value. This is indicated in Table 3. Then having got a higher precision we form the successive differences between the data. It then appears that all these differences can be formulated as multiples of one and the same factor of the order of about 15 kJ mol^{-1}. In the fifth column of Table 3 we indicate the numbers i expressing the multiple in each case. By taking the proper mean of the increments [4, 22] we can obtain a better value of the common factor. It emerges as 15.7 kJ mol^{-1}. Actually, introducing $n = \Sigma i$, one can make a linear regression analysis of the data in columns 3 and 6 of Table 3, which gives

$$\Delta H^{\ddagger} = 2.9 + 15.73\, n \text{ kJ mol}^{-1} \quad (4)$$

n means here the number of vibrational quanta that must be excited to reach the activated state. Realizing

TABLE 2. Activation enthalpy for the reaction $Ni(DMSO)_6^{2+} + L = Ni(DMSO)_5L^{2+} + DMSO$ for various neutral L species. The original data are listed with the unit used in the relevant report, if required kcal mol^{-1} is transformed to kJ mol^{-1}

Exp.	L	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	Reference
(1)	DMSO	8(?)	33(?)	7
(2)			50 ± 2	14
(3)			49.2 ± 0.4	15
(4)			51 ± 3	16
(5)		12.1 ± 0.3	50.6 ± 1.2	21
(6)	pyridine	c. 4	c. 18	7
(7)	terpyridine	15.0 ± 0.7	62.8 ± 2.9	7
(8)	phenanthroline	8.3 ± 0.3	34.7 ± 1.2	7
(9)	bipyridine	12.6 ± 0.1	52.7 ± 0.4	12
(10)			51	18
(11)	pada[a]	12.3 ± 0.4	51.5 ± 1.7	13
(12)	DPAP[b]	16.1 ± 0.9	67.4 ± 3.8	17
(13)	2-aminomethylpyridine	9.1 ± 0.6	38.2 ± 2.3	19
(14)	tetra[c]		47 ± 5[e]	20
(15)	tetra methyl tetra[d]		73 ± 5[e]	20
(16)	4-phenylpyridine	9.0 ± 2	38 ± 8[e]	18
(17)	isoquinoline	7.6 ± 0.2	31.8 ± 0.8	8
(18)	2-(2-aminoethyl)pyridine	12.3 ± 0.2	51.5 ± 0.8	19
(19)	2-(aminomethyl)-6-methylpyridine	14.5 ± 1	61 ± 5[e]	19

[a] Pyridine-2-azo dimethylaniline. [b] 2-(4-Dimethylaminophenilazo)pyridine. [c] 1,4,8,11-Tetraazacyclotetradecane. [d] *N,N',N'',N'''*-Tetramethyl-1,4,8,11-tetraazacyclotetradecane. [e] Discarded in the collation of Table 3 because of the large uncertainty.

TABLE 3. Ordering and arithmetic treatment of the data from Table 2. All units in kJ mol^{-1}

Exp.	$\Delta H^{\ddagger}$	$\Delta H^{\ddagger}_{mean}$	$\Delta(\Delta H^{\ddagger}_{mean})$	$i \times \Delta(\Delta H^{\ddagger}_{mean})$	*n*
(6)	18	18			1
(8)	34.7		16.9	1×15	
(13)	38.2	34.9			2
(17)	31.8				
(2)	50				
(3)	49.2				
(4)	51		16.0	1×15	
(5)	50.6	50.9			3
(9)	52.7				
(10)	51				
(11)	51.5				
(18)	51.5				
(7)	62.8		14.2	1×15	
(12)	67.4	65.1			4
			47.1	3×15	
			$\Sigma\Delta(\Delta H^{\ddagger}_{mean}) = 94.2$ $\Sigma\Delta(\Delta H^{\ddagger}_{mean})/\Sigma i = 15.7$	$\Sigma i = 6$	

this it follows that eqn. (4) is an artefact in the sense that, because of anharmonicity, it should be a second order relation. The available accuracy of the original data (especially for $n = 1$) does not allow such a detailed treatment, however.

The activation enthalpies can thus be expressed in terms of the common factor 15.73 kJ mol^{-1} plus a small constant term that may be due to solvation changes during activation, common to all reactants.

Now transforming the energy increment from kJ mol^{-1} to wave numbers gives us 15.73 kJ $mol^{-1} = 1315$ cm^{-1}. This is seemingly not in agreement with our expectations that the increment should be related to the frequency of the M–O vibration at 444 cm^{-1}. We may now realized, however, that 1315 $cm^{-1} = 3 \times 438$ cm^{-1}. This observation can be interpreted so that the necessary input of energy in every step corresponds to three quanta of the asymmetric M–O vibration.

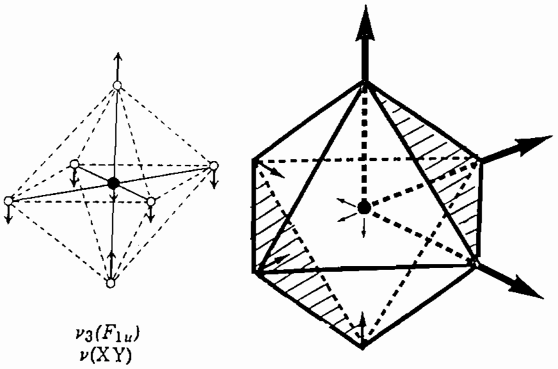

Fig. 2. Schematic view of the ν_3 vibration of an octahedral complex (left figure, reproduced from ref. 24) and the distortion of the octahedron following the combined excitation of the three degenerate modes. The right hand side face is expanding, the left hand side face is contracting.

This might mean that the three degenerate modes of the MO_6 unit are activated together but independently. If they act in phase this will result in a distortion of the octahedron as depicted in Fig. 2. As the major change in any of the three ν_3 vibration modes [24] is an elongation of one of the M—O distances and a corresponding shortening of the opposite bond, it follows that one face of the octahedron is expanding while the opposite is shrinking towards the central metal atom. In this way the expanding face is making it possible for the entering ligand to have space enough to meet the metal atom for binding.

As a corollary one might propose that the larger the incoming ligand is, the larger expansion of the octahedron face is necessary. Consequently the enthalpy of activation will increase with the size (form, bulkiness) of the ligand L. Some indications of this rule may be traced in Table 2.

Conclusions

The perfect agreement between experimental and calculated values for the isokinetic temperature indicates that the model is working well. Actually two cases of sharply defined isokinetic effects can be distinguished: The first case is for perfect resonance, at the minimum of a curve similar to that of Fig. 1. In such a case one can even tolerate a slight spread of the vibrator frequency ω as the minimum is very flat.

The second case is, as in the present study, when the ω value is not very close to the frequency ν but there is a very narrow energy distribution around ω, i.e. the corresponding absorption (emission) band in the IR spectrum is very sharp.

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