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Abstract

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ON THE QUESTION OF THE RELATION BETWEEN THE STABILITY AND REACTIVITY OF COMPLEX COMPOUNDS

Hertz recently published an interesting paper on the determination of the rate of exchange reactions in complex ions on the basis of the width of nuclear magnetic resonance lines (1).

This paper gives numerical data on the magnitudes of the rates of the formation and dissociation reactions of a whole series of complex bromides and iodides derived from divalent mercury, cadmium, and zinc in aqueous solutions. The author came to the conclusion that, in general, recombination of the constituent parts of a complex ion proceeds the faster the smaller the corresponding instability constant, i.e., the stronger the corresponding complex. At the same time it was shown that the processes of isotopic exchange in the stronger mercury complexes proceed appreciably faster than in the less stable cadmium complexes. In presenting these very interesting data, Hertz nowhere mentions the work carried out in our laboratory, despite the fact that these works are widely cited in the foreign literature (2). Meanwhile, a comparison of the data mentioned appears highly expedient.

In 1949, in a joint paper with L. E. Nikol' skaya (3), the opposition between thermodynamic stability and kinetic lability was first discovered for compounds of the composition $K_2[PtX_4]$, where $X = \mathrm{Cl, Br, J, CN}$. The rate of isotopic exchange increases along the series $\mathrm{Cl} < \mathrm{Br} < \mathrm{J} < \mathrm{CN}$, i.e., it increases in going from the thermodynamically least stable complexes to the most stable ones. This peculiar behavior was associated with the fact that in the series $\mathrm{Cl, Br, J, CN}$ there is both an increase in the trans influence of the ligands and an increase in the tendency toward complex formation with the Pt^{II} ion. Somewhat later, in papers by A. Adamson and co-workers (4), as well as by MacDiarmid and Hall (5), it was likewise pointed out that, generally speaking, there may be no correspondence between the thermodynamic stability of a complex, measured by the magnitude of the instability constant, and the rate of isotopic exchange.

However, in the above-mentioned paper (3) it was established not only that there is no correspondence between the magnitudes of the instability constants and the rate of isotopic exchange, but that there is a direct opposition between them: the stronger the complex, the faster the exchange. It subsequently turned out that such an opposition is characteristic of complex compounds of Pt^{II} containing acidic residues labilized by trans-active ligands situated opposite them.*

This could be clearly shown by using the rate constants, obtained by us and partly by other authors, for the substitution reactions of coordinated chlorine and bromine in derivatives of Pt^{II}, as well as the values, obtained by me together with G. A. Shagisultanova (^{7}) and M. I. Gel' fman (^{8}), of the partial and overall instability constants of numerous Pt^{II} derivatives.

* In compounds in which chlorine is situated opposite very weakly trans-influencing ligands, in particular in the ion $[Pt(NH_3)_3Cl]^+$, and also in the ions of composition $[Pt(NH_2CH_2CH_2NHCH_2CH_2NH_2)Cl]^+$, studied by Basolo, Pearson, and Gray (^{6}), on the contrary, there is a direct correspondence between the stability of the complex and the rate of substitution reactions, i.e., the rate is the lower the stronger the complex.

In Table 1 we give data on experimentally determined rate constants for activation reactions of Pt^II complex compounds forming the Werner-Miolati series, as well as the corresponding values of the instability constants at 25°C.

Both the kinetic and the thermodynamic data refer to the process of substitution of one chlorine (or bromine) atom in the indicated complexes. Table 1 gives the values of the instability constants k_4^{-1}, the rate constants of activation (substitution of chlorine or bromine by a water molecule), k_1, and also of the reverse reaction of substitution of the water molecule by, respectively, the chlorine or bromine ion, k_2.

Table 1

Complex	$PtCl_4^{2-}$	$PtNH_3Cl_3^-$	NH_3 Cl NH_3 Pt	NH_3 Cl CCl Pt	$Pt(NH_3)_3Cl^+$ NH_3	$PtBr_4^{2-}$
k_4^{-1}, M	$2 \cdot 10^{-2}$	$1,2 \cdot 10^{-2}$	$\sim 4 \cdot 10^{-3}$	$0,8 \cdot 10^{-3}$	$2,5 \cdot 10^{-4}$	$3 \cdot 10^{-3}$
k_1, sec^{-1}	$0,4 \cdot 10^{-4}$	$0,6 \cdot 10^{-4}$	$0,38 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$0,22 \cdot 10^{-4}$	$1,6 \cdot 10^{-4}$
k_2, $M^{-1} \cdot sec^{-1}$	$0,22 \cdot 10^{-2}$	$0,5 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$1 \cdot 10^{-1}$	$1,1 \cdot 10^{-4}$	$5,3 \cdot 10^{-2}$

Analyzing these data, one can see that the rate of entry of H_2O (and then also OH) into the indicated ions is maximal in the case of trans-$Pt(NH_3)_2Cl_2$ and minimal in the case of $Pt(NH_3)_3Cl^+$. In the presence of the trans-active coordinate Cl—Pt—Cl, the constants k_1 for the rate of substitution of chlorine by water, although not very strongly, nevertheless exceed the values of the corresponding constants for compounds that do not contain the coordinates Cl—Pt—Cl and Br—Pt—Br.

For $PtBr_4^{2-}$, k_1 is 4 times greater than for $PtCl_4^{2-}$. This reflects the Chugaev trans effect. The circumstance that k_1 for $PtNH_3Cl_3$ is one and a half times greater than for $PtCl_4^{2-}$ reflects the cis effect described by us in work with Yu. N. Kukushkin (^{9}) and D. B. Smolenskaya (^{10}), i.e., a change in the magnitude of the trans influence on the coordinate X—Pt—X under the influence of a cis substituent, in this case an ammonia molecule. In previously published works, experimental data are contained which show that the same arrangement of complexes according to the magnitudes of the rate constants also holds for bimolecular reactions of interaction of these complexes with NH_3 and certain other amines, although the constants differ in dimension and in absolute values.

Along with this, what is striking is the opposition, occurring for all the complexes listed except $Pt(NH_3)_3Cl^+$, between the activation rate constants and the instability constants. In other words, here too, the stronger the complex, the faster the substitution proceeds. Such, in any case, is the situation for all Pt^II complexes containing trans-active coordinates.

In one of the previously published papers I already gave an explanation for this, at first sight paradoxical, relationship. The point is that the trans and cis effects, exerting an accelerating action on the processes of substitution of chlorine or bromine at the coordinates X—Pt—X (where X = Cl or Br), to an even greater degree labilize the trans-positioned H_2O molecule, which, in combination with the greater (compared with H_2O) tendency of Br^- and Cl^- ions toward non-ionogenic combination with Pt^II, determines the greater rate of reverse entry of the corresponding ions into the initial complex. Meanwhile, the instability constant k_4^{-1}, as is known, is equal to the ratio of k_1 (the rate of dissociation of the complex) to k_2 (the rate of recombination or formation of the corresponding complex).

A small value of the instability constant, in other words the strength of the complex, indicates a sharp predominance of the rate of formation of the complex over the rate of its dissociation.

In turn, this indicates a much greater probability of the presence of the Me–X bond as compared with the Me–H_2O bond.

Indeed, the dissociation reaction of the complex is accompanied (or caused) by interaction of the complex with water. If the concentration of the complex solution is 10^{-3}, then the ratio of the active masses of water and of the complex is approximately $5.5 \cdot 10^4$. Even with such an enormous excess of water, the rate of the dissociation reaction is much lower than the rate of interaction of the aquo ion with the X^- ions initially present in the dissolved complex and displacing the water molecule in accordance with the SN_2 mechanism. Platinum complexes are relatively inert, and against this background intramolecular trans- and cis-effects show up quite distinctly.

If, however, the rates of dissociation and especially of formation of complexes are very high (the complexes are very labile), then even without the participation of intramolecular kinetic effects, solely because of the greater tendency of X^- ions toward complex formation with the metal ion, the situation established by us in

1949 for PtX_4^{2-} ions and confirmed by Gerdes for derivatives of Hg^{II} and Cd^{II} may still occur, namely: the stronger the complex, the faster the exchange.

In 1960, in a joint study with V. E. Mironov (^{11}), we attempted to verify this relationship specifically for salts containing the ion HgX_4^{2-}, where $X = Cl, Br, J, CN$. However, this attempt was unsuccessful, since in all these systems isotopic exchange proceeded practically instantaneously, and the usual method for studying the exchange rate was ineffective. Gerdes succeeded in finding that the rate constants for dissociation of the ions $HgBr_3^-$ and $HgBr_4^{2-}$, according to the equations:

$$HgBr_3^- \rightleftarrows HgBr_2 + Br^-,$$

$$HgBr_4^{2-} \rightleftarrows HgBr_3^- + Br^-$$

are equal to $2.5 \cdot 10^7$, while the constants of the reverse recombination reactions are, respectively, $6.4 \cdot 10^9$ and $4.6 \cdot 10^8$ (calculated from the instability constants determined by Sillén).

Table 2

Instability constants of the ions HgX_4^{2-} and PtX_4^{2-}

Ion	β_4^{-1}	k_4^{-1}	Ion	β_4^{-1}	k_4^{-1}
$HgCl_4^{2-}$	$9 \cdot 10^{-17}$	$\sim 10^{-1}$	$PtCl_4^{2-}$	$2.5 \cdot 10^{-17}$	$1.7 \cdot 10^{-2}$
$HgBr_4^{2-}$	$2.3 \cdot 10^{-22}$	$\sim 5 \cdot 10^{-2}$	$PtBr_4^{2-}$	$4 \cdot 10^{-21}$	$0.3 \cdot 10^{-2}$
HgJ_4^{2-}	$5.2 \cdot 10^{-31}$	$5.9 \cdot 10^{-3}$	PtJ_4^{2-}	$2.5 \cdot 10^{-30}$	–
$Hg(CN)_4^{2-}$	$3.2 \cdot 10^{-42}$	$1 \cdot 10^{-3}$	$Pt(CN)_4^{2-}$	$1 \cdot 10^{-41}$	–

We have already previously noted the close correspondence between the instability constants of the PtX_4^{2-} and HgX_4^{2-} systems, which is quite clearly seen from the appended Table 2, and at the same time the enormous difference in the kinetic character of these systems was emphasized.

With the aid of Gerdes' data this difference can be expressed quantitatively. Thus, for $PtBr_4^{2-}$

$$k_4^{-1} = 3 \cdot 10^{-3} = \frac{1.6 \cdot 10^{-4}}{5.3 \cdot 10^{-2}},$$

whereas for $HgBr_4^{2-}$

$$k_4^{-1} = 5 \cdot 10^{-2} = \frac{2.5 \cdot 10^7}{4.6 \cdot 10^8}.$$

Using Gerdes' method, one can again try to compare the rates of isotopic exchange in the ions $HgBr_4^{2-}$ and HgJ_4^{2-} (and perhaps also $HgCl_4^{2-}$) and

in this way, to test whether the relationship is also obeyed for Hg^II derivatives: the stronger the complex, the faster the exchange.

However, the data already obtained by Hertz indicate that the opposition we found for Pt^II derivatives between thermodynamic stability and kinetic lability may also occur for certain derivatives of other metals.

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Note: Figure translations are in progress. See original paper for figures.