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The Application of Mössbauer Spectroscopy to the Study of Tin-containing Catalysts

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The principal problems arising in the study of tin-containing homogeneous and heterogeneous catalysts by Mössbauer spectroscopy are reviewed. The information provided by the parameters of the method, among which special attention has been devoted to the probability of the resonance absorption of γ-quanta by the specimen and its temperature variation, is analysed. The principal results obtained in the study of the structure and properties of various tin-containing catalysts are surveyed.
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I. INTRODUCTION

Specific types of tin(II)-containing compounds have now gained a firmly established place among homogeneous and heterogeneous catalysts of various processes in reductive media. $SnCl_3$-containing transition metal complexes are most widely used as homogeneous catalysts. Platinum metal complexes, both those in which the ligands are tin halide species alone and complexes containing PR_3, $P(OR)_3$ and CO molecules in addition to Cl and $SnCl_3$, exhibit catalytic properties in the hydrogenation reactions of various monoolefins and polyolefins as well as unsaturated organic acids, in their isomerisation, in olefin carboxylation processes, etc. Most detailed information on this question has been published by Matvienko.[1] On the other hand, industrial catalytic processes are mainly carried out on deposited Pt–Sn intermetallic compounds, which are used in reforming[2] and dehydrogenation[3] processes.

The unique possibilities of the Mössbauer method for securing information about the structure and properties of tin-containing compounds have been known for a long time.[4] However, its application to the study of such catalysts has been inadequately dealt with in review articles. One of the first reviews in which questions concerning the application of Mössbauer spectroscopy to catalysis were discussed dealt largely with iron compounds[5] and concentrated mainly on two possible aspects of the application of the Mössbauer effect: (1) the derivation of information about the electronic states of the atoms in catalysts and about the relation with their activity and selectivity; (2) the detection of intermediate complexes in catalysis. The only study considered by Gol'danskii and Suzdalev[5] was that of Skalkina et al.[6], who found that the relation between the rate of the oxidative ammonolysis of propene and quadrupole splitting Δ (for a constant chemical shift δ) has an extremum for SnO_2 and its solid solutions in Sb_2O_4, MoO_3, and Fe_2O_3.

The most complete review, in the sense of coverage of problems involving catalysis, is that of Dumesic and Topsoe,[7] who discuss in detail the information contained in the parameters of the Mössbauer spectra, the characteristic features of the application of the method to the study of the structure of the catalyst surface, the adsorption of various molecules on such a surface, and the reactivity of molecules containing different Mössbauer atoms. Their review covers an even greater number of examples of the study of tin-containing catalysts, but these are mainly tin(IV) compounds. In a later review[8] dealing with the application of Mössbauer spectroscopy to catalysis, no information whatever is included about tin-containing catalysts. Finally, the compilations of communications on Mössbauer spectroscopy, regularly published in the journal Analytical Chemistry (R) (see, for example, Stevens et al.[9]) are concerned with all the aspects of the application of the method and do not analyse the characteristics of its application to the study of particular types of systems, including catalysts.

This position can be partly accounted for by the fact that the number of studies on tin-containing catalysts by the Mössbauer method has indeed been small. For example, the first investigation of the industrial tin-containing catalysts deposited on γ-Al_2O_3 appeared in 1975.[10] The authors[10] showed that the surface of the carrier contains a whole set of tin (IV), tin(II), and zerovalent tin compounds, although the main problem is their detailed identification. Studies of this kind have been partly discussed in a recently published review,[11] but the methodological aspect of the problem of the determination of the number of individual components of the catalyst, their composition, and their state on the basis of the complex overall Mössbauer spectrum remained inadequately dealt with.

The experience gained in the application of physical methods to catalysis, accumulated at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, has shown that a fairly profound understanding of the reaction mechanism and of the action of the active centre has been achieved in those cases where it was possible to obtain reliable information about its composition, structure, or the type of compound or phase constituting this centre. One must note that none of the reviews published hitherto has considered the outcome of the application of the Mössbauer effect to the study of tin-containing homogeneous catalysts. Here too it is necessary to obtain in the first place information about their composition and structure. In view of the foregoing, in the present review we shall consider primarily the structural aspect of the application of the Mössbauer method to the study of tin-containing homogeneous and heterogeneous catalysts.

II. METHODOLOGICAL PROBLEMS IN THE STUDY OF CATALYSTS BY THE MÖSSBAUER METHOD

In this Section, no attempt is made to describe all the methodological problems of the application of the Mössbauer effect in chemistry; like the theory of the method, they have been described in detail elsewhere.[12-16] Here we shall deal only with those of their aspects which are most important for the investigation of catalysts.

1. Homogeneous Systems

As mentioned above, the homogeneous catalysts usually consist of $SnCl_3$-containing platinum metal complexes as well as clusters of the same metals incorporating $SnCl_3$, $SnCl_2$, and SnCl groups and Sn atoms.[1,17,18]

It has been shown[17-20] that the line form in the Mössbauer spectra of complex compounds frequently differs from the ideally symmetrical doublet; this can be caused by the non-equivalence of the positions (and hence the electronic structures) of the $SnCl_3$ ligands in the coordination sphere of the platinum metal or, which happens more frequently, by the presence in its coordination sphere of tin-containing ligands of different composition. The latter is typical for clusters.[17,18,21] In this case the determination of the parameters of the Mössbauer signal of each kind of tin-containing groups makes it necessary to resolve the overall spectrum into individual doublets with a Lorentzian line form. Fig. 1 (Yurchenko[18]) presents the Mössbauer spectrum of the $[Pd_3Sn_8Cl_{20}]^{4-}$ cluster obtained in the form of the tetraphenylphosphonium salt; the spectrum was interpreted on a BESM-6 computer. The line form of each quadrupole doublet was described by the expression

$$W_a(E) = \frac{1}{2\pi}\left[\frac{\Gamma_{nat}/2}{(E-E_0-\Delta)^2+(\Gamma_{nat}/2)^2}+\frac{\Gamma_{nat}/2}{(E-E_0+\Delta)^2+(\Gamma_{nat}/2)^2}\right], \quad (1)$$

where E is the energy of the emission of γ-quanta, E_0 the energy of the resonance transition, and Γ_{nat} the natural line width.

Later it was found that it was more rational to carry out an analogous resolution procedure with the aid of an SK-2 curve synthesiser,[18] which makes it possible to isolate simultaneously up to seven components of the spectrum. The area under the envelope of each doublet is related to the number of absorbing atoms n by the familiar expression[14,15,17]

$$S_9 = \frac{\pi}{2}\Gamma_{nat}\sigma_0 \varkappa f n f', \quad (2)$$

in which $\varkappa f$ can be determined by the black absorber method, which has been described for tin.[22] Yurchenko[18] adopted $f'_{77} = 0.22$ for the $SnCl_3$ ligand, 0.3 for SnCl, and 0.4 for Sn in the Pd_3Sn alloy.[23] Taking into account these values of f' for Sn in $[Pd_3Sn_8Cl_{20}]^{4-}$, it is found that the ratio of the areas of the two doublets in Fig. 1 corresponds to the ratio of the numbers of tin atoms in the ligands of the cluster, which is 3:1;[18,21] this constitutes one of the arguments in support of the representation of the composition of the cluster by $[Pd_3(SnCl_3)_6(SnCl)_2]^{4-}$.[21]

The study of the state of catalysts under the conditions of the catalytic process (*in situ*) is particularly valuable. For homogeneous systems, this requires the measurement of the Mössbauer effect for solutions, which, by virtue of the nature of the effect itself, becomes possible only when the latter are frozen. In those cases where the concentration of the catalytically active forms of the complex or intermediate states is high, freezing of the solutions has a conserving effect on these forms and makes it possible to identify them from the Mössbauer spectra. However, studies available hitherto on the Mössbauer spectroscopy of frozen solutions have been associated mainly with the analysis of complex formation processes.[24-27] In their methodological aspect, such studies require the availability of cells of appropriate design, which would not break on cooling the solution to the temperature of the liquid nitrogen and would retain their hermetic seal.

The use of Mössbauer parameters such as δ and Δ for the identification of the types of complexes predominating in solution required the accumulation of information about the characteristics of the Mössbauer effect for compounds of tin in various oxidation states and with different structure of its immediate environment. For tin(II) complexes, such a study has been carried out[18] and the relation between the observed changes in the Mössbauer parameters and the characteristics of the structure of the complex as a whole and of the tin(II)-containing ligands in it has been elucidated by simultaneous investigation of the crystals of the complexes by the X-ray diffraction and Mössbauer spectroscopic methods. Fig. 2 presents examples of the Mössbauer spectra of various tin compounds; evidently, the values of δ, Δ, the width of the components Γ, and the form of the spectra are sensitive not only to changes in the oxidation state of tin but also to the characteristics of the structure of the tin-containing compounds.[17] Thus the formation of a coordinate bond by the $SnCl_3$ group alters δ from 3.64–3.00 mm s^{-1} and Δ from 0.90–1.73 mm s^{-1} for the $SnCl_3^-$ ion[28] to 1.50–1.95 mm s^{-1}

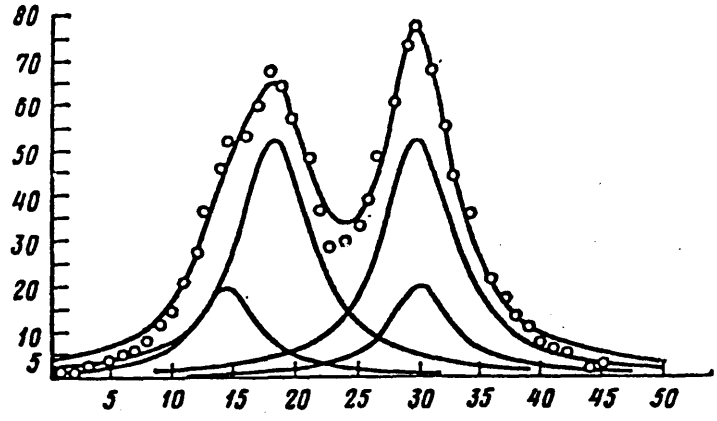


Figure 1. The Mössbauer spectrum of the $(Ph_4P)_4[Pd_3Sn_8Cl]_{20}$ cluster (in terms of the arbitrary units of the graph plotter.

and 1.60–2.10 mm s^{-1} respectively.[29–35] If all the $SnCl_3$ ligands in the coordination sphere of the complex have equivalent positions and geometries, as, for example, in $[PdCl_3(SnCl_3)]^{2-}$ (Fig. 2, curve *3*), then under these conditions a symmetrical doublet is observed with lines of equal and minimum width. If the ligands in the coordination sphere of the complex occupy non-equivalent positions, for example, the axial and equatorial $SnCl_3$ groups in $[Pt(SnCl_3)_5]^{3-}$, and therefore have different values of δ and Δ, then the overall spectrum can be asymmetric and can have broader lines (Fig. 2, curve *4*). Finally, the presence of tin(II)-containing ligands in the complex which are non-equivalent as regards composition and structure imparts a strongly asymmetric contour to the overall spectrum resulting from the doublets due to each ligand (Fig. 2, curve *5*).

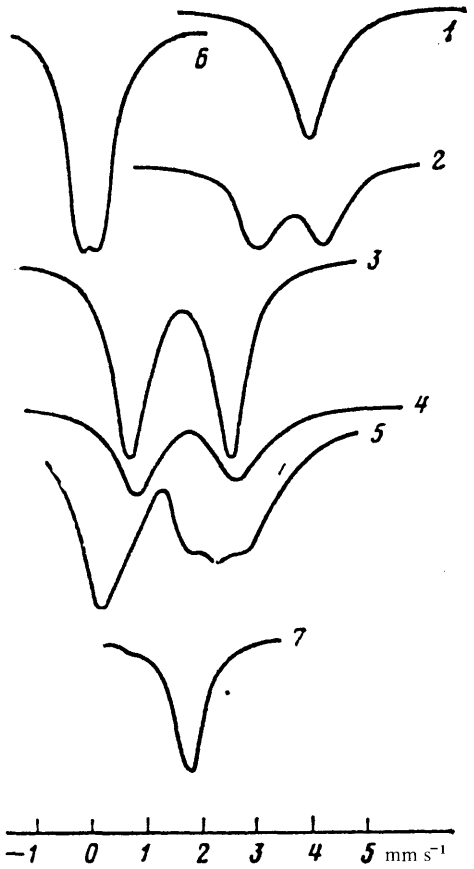


Figure 2. Mössbauer spectra: *1*) $SnCl_2$(anh.); *2*) $SnCl_2 \cdot 2H_2O$; *3*) $(Ph_4P)_2[PdCl_3(SnCl_3)]$; *4*) $(Et_4N)_3[Pt(SnCl_3)_5]$; *5*) $Cs_4[Rh(Sn_4F_{15})(SnF_2(H_2O)_2]_2 \cdot 2H_2O$; *6*) SnO_2; *7*) PtSn.

The non-equivalence of the $SnCl_3$ ligands as regards their positions in the coordination sphere of the complex affects the form of the spectrum to a greater extent than the differences between the geometries of each of them. This has been demonstrated by an investigation[36] of the crystal structure and spectra of $[Me_4N]_4[OsCl(SnCl_3)_5]$. All ten crystallographically independent $SnCl_3$ ligands in the unit cell of the crystal of this compound have appreciably different SnCl bond lengths and Cl–Sn–Cl angles. Nevertheless, the Mössbauer spectrum of the powdered complex consists of a symmetrical doublet;[32] the above differences in the geometry of the $SnCl_3$ groups induce only a broadening of the line widths to 0.85 mm s^{-1}.

Thus the results of a number of studies[30–36] helped to discover how much structural information is contained in the Mössbauer characteristics of tin(II) compounds, such as the form and width of the components of the recorded spectrum and the values of δ and Δ for its individual components. Dynamic parameters, particularly f', have not been used to characterise the structural features of tin-containing catalysts.

The quantity f' is defined by the expression

$$f' = \exp\left(-\frac{\langle x^2\rangle}{\lambda^2}\right), \qquad (3)$$

where $\langle x^2\rangle$ is the mean square shift of the emitting nucleus at the crystal lattice site in the direction of the stream of γ-quanta. $\lambda = \lambda/2\pi$, and $\lambda = 0.52$ Å for ^{119}Sn. One might expect that the characteristics of the structure of tin-containing compounds will be reflected in the value of $\langle x^2\rangle_{Sn}$ for the latter and hence in the value of f'.

The parameter f' is, in principle, related to the macroscopic properties of the entire crystal containing the Mössbauer atom.[13,14] The value of f' in the range $1 \leq f' \leq 0$ depends on whether there exist in the given crystal possibilities for the consumption of part of the energy of the γ-quanta, which is equal to the recoil energy of the Mössbauer nucleus. Such energy dissipation channels are provided by the excitation of the phonon spectrum and of the individual vibrations of the crystal in the optical branches.[37,38] In simplest cases of one- or two-atom lattices, the Debye model of the solid is used for the description of f',[39] according to which we have in the temperature range above 77 K

$$f' = \exp\left(-\frac{6E_R T}{k\Theta^2}\right), \qquad (4)$$

where Ξ is the characteristic Debye temperature for the crystal, E_R the recoil energy, and $k\Xi = \hbar\omega_{max}$.[12–14] It has been suggested that, when the Mössbauer nucleus in the solid forms part of the composition of the molecule or ion having characteristic vibration frequencies ω_i, Einstein's model of the solid be employed, according to which

$$f' = \prod_i \exp\left(-\frac{E_R}{\hbar\omega_i}\coth\frac{\hbar\omega_i}{2kT}\right). \qquad (5)$$

It has also been suggested[40] that f' for molecular crystals be expressed as the product $f'_{ia}f'_{ir}$, where f'_{ia} characterises the component of the probability of the absorption of a γ-quantum which depends solely on the intramolecular vibrations of the Mössbauer atom, while f'_{ir} characterises the part which depends on the vibrations in the solid of the entire molecule containing the given atom. Eqn. (3) is then valid for f'_{ia} and f'_{ir} separately, $\langle x^2\rangle_{ir}$ is a result of the shift of the Mössbauer atom as a consequence of intermolecular vibrations, and $\langle x^2\rangle_{ia}$ is the result of the shift due to intramolecular vibrations. A number of compounds, for example organotin(IV) compounds, have high frequencies (300–400 cm^{-1} and above) and, in conformity with Eqn. (4) or (5), $f'_{ia} \to 1$. Debye's model of the solid state is usually employed to describe f'_{ir} and the following relation is analysed:

$$\frac{d\ln f'}{dT} = \frac{3E_0^2 k}{M_{eff}c^2\hbar^2\omega_i^2}, \qquad (6)$$

where M_{eff} is the mass of the entire molecule and ω_i its

vibration frequency (the lowest lattice vibration frequency is adopted as ω_i). In combination with the determination of ω_i from Raman spectra, this approach has been used in a whole series of studies, for example, for the determination of the molecular weights of tin-containing compounds.[41-45]

It follows from Eqns.(4)–(6) that the higher the effective mass of the vibrating molecule and the lower the vibrational frequency of the Mössbauer atom, the closer is f' to unity and the weaker the dependence of f' on T.

However, the above approach proved to be unsuitable for a whole series of systems. For example, in biological objects containing the ^{57}Fe label a marked dependence of f' on T (over a limited temperature range) and of the absolute value of f' on the water content in the protein has been observed.[46,47]

It is also noteworthy that, in an early study[48] of the Mössbauer effect in amorphous tin halide compounds, it was observed that the absorption of γ-quanta without recoil does not require the presence of a crystal structure as such. It is only necessary that an effective mechanism hindering the consumption of the energy of the γ-quanta in the form of the recoil energy in different kinds of low-frequency rotational and vibrational movements of the groups containing the Mössbauer atom should operate.

In terms of the structural aspects of the use of Mössbauer spectroscopy in which we are interested, it was extremely important to elucidate to what extent the parameter f' itself and its dependence on T are determined by the internal structure of the tin-containing molecule and why this is so. In order to solve such a problem, it is essential to have information about the crystal structures of various tin(II) halide complexes of transition metals. Such data have been obtained in a number of studies.[19,36,49-53] They show that all tin-containing halide complexes without exception are constructed according to the principle of molecular crystals, i.e. the interaction energies of the atoms within the complex anion and within the cation (short interatomic contact) greatly exceed the energy of interaction between them (long interatomic contact). The structure of the (Sn–F)-containing anion is such that four Sn atoms are linked via bridging F atoms. In the chlorine complexes tin is present in the form of the $SnCl_3$ ligand, but the geometry of the latter within the anion and within the unit cell and also in different compounds can vary significantly.

A study[17,54] of f' and of its dependence on T for the number of (Sn–F)-, (Sn–Cl)-, and (Sn–Br)-containing complexes has shown that the maximum values of f' and its weakest temperature dependence ($f'_{77} = 0.5$, $f'_{77}/f'_{153} = 1.6$),† close to that obtained for platinum–tin and nickel–tin alloys, are observed for the fluorides. For the $SnCl_3$-containing complexes, the values of f' are lower and their dependence on T is more marked ($f'_{77} = 0.2$, $f'_{77}/f'_{153} \cong 4-5$). For the $SnBr_3$-containing analogues with the same cations, the values of f'_{77} are somewhat greater (0.3), but the dependence of f' on T is steeper ($f'_{77}/f'_{153} \cong 6$). In a series of compounds of the same $SnCl_3$-containing complex anion, the increase of density from 1.8–2.2 g cm^{-3} to 3.3 g cm^{-3} on replacement of the bulky organic cation by Cs^+ entails an increase of f'_{77} to 0.4 and a weakening of its temperature dependence ($f'_{77}/f'_{153} = 3$); however, in this case too f' is smaller and its dependence on T is stronger than for the fluorides. For frozen fluoride solutions, the values of f' are also higher than for the chlorides. This demonstrates that the measured f'_{eff} for the crystalline complexes investigated depend both on the internal properties of their tin-containing anions and on the characteristics of the interionic interaction in the crystal as a whole, i.e. both on f'_{ia} and on f'_{ir}.

The components of the effective mean-square vibration amplitude of the tin atom in the crystal lattices of such ($\langle x^2\rangle_{eff}$) have been analysed:[55]

$$\langle x^2\rangle_{eff} = \langle x^2\rangle_{ia} \coth\frac{\alpha_{ia}}{T} + \langle x^2\rangle_{i\gamma} \coth\frac{\alpha_{i\gamma}}{T}, \qquad (7)$$

where $\alpha_{i(j)} = \hbar\omega_{i(j)}/2k$, ω_i the frequency of the lowest-frequency vibration of the Mössbauer atom within the molecule, and ω_j the frequency of its vibration together with the molecule. This equation was first used to analyse the dynamics of the behaviour of the tin atom on the silica gel surface.[56]

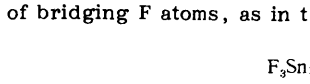
The observed[55] $\langle x^2\rangle_{eff}$–T relations are illustrated in Fig.3; Table 1 presents the parameters and the temperature ranges in which these relations were fitted by Eqn.(7). The effective frequencies of the vibrations of the ^{119}Sn atoms within the anion and of the associated vibrations have been calculated from the $\langle x^2\rangle$ obtained. The frequencies ν_{ir} are reasonably consistent with the vibrations of species having masses greater than 1000 a.m.u. and weakly linked to one another. They have similar values for all solid halides except complex 2. This is consistent with the crystallographic data, according to which the distances between the atoms in compound *1* are $R(Sn - Cs^+) > 4.5$ Å and $R(F - Cs^+) > 3$ Å and differ little from the distances between the atoms of the $SnCl_3$ and $(CH_3)_4N$ groups in compound *3*.[49-53] The effective intermolecular vibration frequencies decrease in the sequence F > Cl > Br, remaining higher in absolute magnitude than the observed low-frequency components of the spectrum.

Table 1. Parameters obtained by fitting Eqn.(7) to the curves in Fig.3.[55]

Complex*	T, K	$10^{18}\langle x^2\rangle_{ia}$, cm^2	$10^{18}\langle x^2\rangle_{ir}$, cm^2	α_{ia}, K	α_{ir}, K	ν_{ia}, cm^{-1}	ν_{ir}, cm^{-1}
1	77–300	0.04	0.27	20	100	350	4.7
2	77–160	0.07	0.1	10	100	200	12.7
3	77–140	0.08	0.25	8	120	175	5.0
4	77–140	0.10	0.15	10	120	140	5.6
5	77–140	0.05	0.55	25	100	280	2.3

*The numbers of the complexes correspond to the numbers of the curves in Fig.3.

The calculation,[55] based on the measured force constants of the SnX_3^- anions[57] and the complex $[PdCl_3(SnCl_3)]^{2-}$ [50] as well as the available information about the geometry of the complexes,[19,36,49-53] made it possible to discover a series of important characteristic features of the compounds considered. Firstly, the number of low-frequency (up to 100 cm^{-1}) normal vibration modes increases in the sequence F, Cl, Br: 55 cm^{-1} for the F-derivatives, 61, 66, 75, and 82 cm^{-1} for the Cl-derivatives, and 44, 52, 73, 85, 90, 97 cm^{-1} for the Br-derivatives. Secondly, in the presence of bridging F atoms, as in the fragment



the calculated $\langle x^2\rangle$, corresponding to a frequency of 55 cm^{-1}, is 11.6×10^{-20} cm^2, while without a bridging atom, as in the fragment, $F_3Sn-M-SnF_3$, it amounts to 30.6×10^{-20} cm^2 at a

†The subscripts f' correspond to the temperatures of the measurement (K).

frequency of 74 cm^{-1}. Thirdly, the tin atom undergoes the greatest shift in stretching vibrations [ν(SnX) whose observed frequencies decrease in the same sequence of atoms X (524 cm^{-1} for F, 316 cm^{-1} for Cl, and 225 cm^{-1} for Br). The calculated values of f^*_{ia} at $T = 0$, expressed as the product of the f'_{ia} for each of the frequencies quoted above, proved to be 0.64 for the fluorides, 0.58 for the chlorides, and 0.46 for the bromides.

Table 2 presents the values of f'_{ia} and f'_{ir} as well as their temperature variations obtained by Eqns. (3) and (7) and taken from Yurchenko et al.[55] Comparison of the values of f'_{ia} at $T = 0$ with those of the f^*_{ia} listed above shows that the analysis of the vibrations of the metal–tin halide complexes made it possible to estimate correctly their characteristic values of $\langle x^2\rangle_{ia}$ ($T = 0$) and the corresponding f^*_{ia}.

The analysis suggested[56] that all the low-frequency vibrational modes, including ν(SnX), contribute effectively to the mechanism of the changes in f'_{eff} in the series of tin(II) halide-containing complexes of transition metals, the increase of the number of such modes from X = F to X = Br and the decrease of ν(SnX) in the same series having the greatest importance. The data of Yurchenko et al.[55] have shown that the values of f' characteristic of the SnX_3 ligands occur in the range 77–140 K; they differ little in the series of metals and can be used to analyse the type of tin-containing halide complexes obtained. Table 2 also shows that at $T = 0$ the overall value of f'_{eff} is approximately equally determined by the presence of zero-point vibrations of the tin atom in the anion and associated vibrations of the anion. An increase of temperature, within the limits where Eqn. (7) fitted to the relations shown in Fig. 3 holds, leads to a greater intensification of the internal vibrations of the tin atom, so that along these sections the temperature dependence of f' is determined mainly by the internal properties of the anions. The characteristics of the packing and of the interionic interaction have a greater influence at higher temperatures.

Table 2. Temperature dependence of the parameters f'_{ia} and f'_{ir} for the complexes.

T, K	f'_{ia}	f'_{ir}	T, K	f'_{ia}	f'_{ir}
$Cs_4[RhSn_4F_{15}(SnF_2\cdot 2H_2O)_2]$			$(Me_4N)_4[OsCl(SnCl_3)_5]$		
0	0.94	0.67	0	0.89	0.69
77	0.79	0.63	77	0.32	0.67
140	0.66	0.52	140	0.13	0.59
300	0.42	0.29			
$Cs_3[Pt(SnCl_3)_5]$			$(Me_4N)_4[OsBr(SnBr_3)_5]$		
0	0.90	0.86	0	0.86	0.80
77	0.45	0.84	77	0.32	0.79
140	0.26	0.78	140	0.13	0.73

It was noted above that the establishment of the dependence of the rate and selectivity of a catalytic reaction on the electronic structure of the catalyst atoms was already identified in an earlier review[5] as one of the most important aspects of the application of the Mössbauer effect in catalysis. Unfortunately, so far the study of Skalkina et al.[6] is perhaps the only one where such an attempt was made in relation to a heterogeneous catalytic process. We are unaware of any studies on these lines in relation to homogeneous catalysis. The reason is primarily that, despite the extensive literature describing the catalytic reactions in the presence of $SnCl_3$-containing complexes,[1,18] not even the

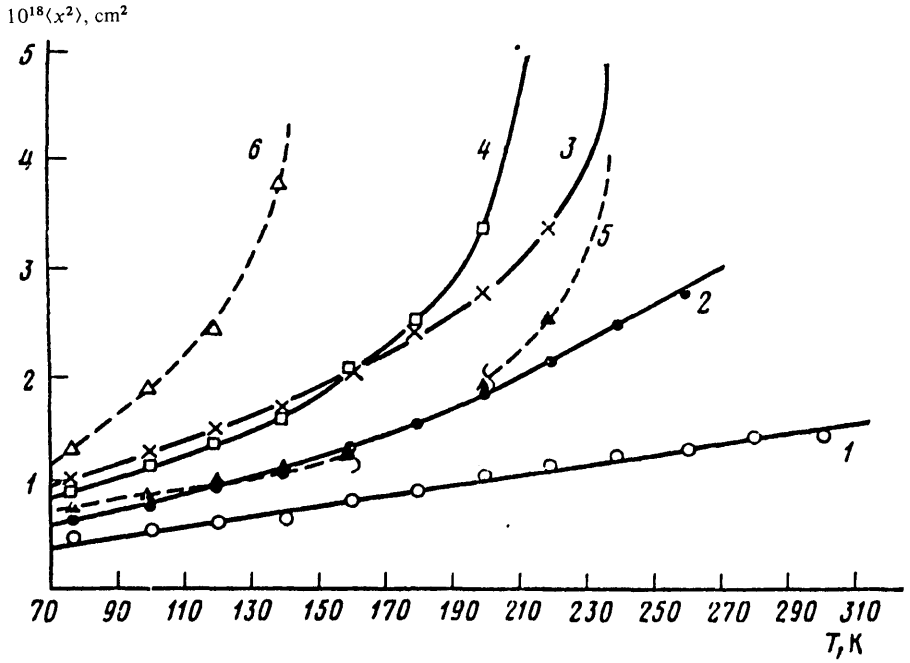


Figure 3. Temperature dependence of the effective mean square amplitudes of the shifts of the ^{119}Sn atoms in tin halide catalysts: *1*) $Cs_4\{Rh(Sn_4F_{15})[SnF_2(H_2O)_2]_2\}\cdot 4H_2O$; *2*) $Cs_3[Pt(SnCl_3)_5]$; *3*) $(Me_4N)_4[OsCl(SnCl_3)_5]$; *4*) $(Me_4N)_4[OsBr(SnBr_3)_5]$; *5*) $[RuSn_3F_{18}]^{4-}$ solution in 3 M HF (0.015 M); *6*) $[Pd(SnCl_3)_5]^{3-}$ solution in 3 M HCl (0.032 M).

composition of the complex functioning as the true catalyst has been elucidated in any of the studies except those in Refs.1, 18, 58. At the same time, other causes limiting the extensive possibilities for the determination of the electronic structure of the tin atoms in tin-containing homogeneous complexes provided by the analysis of Mössbauer spectroscopic parameters such as δ and Δ have also been noted.[18] The first parameter is related to the spherical symmetry of the electron density distribution around the nucleus of the tin atom:[14]

$$\delta = C\frac{\Delta r}{r}\Delta|\psi_{ns}|^2 , \qquad (8)$$

where C is a constant characterising the Mössbauer nucleus, Δr the difference between the radii of the nuclei in the ground and excited states, r the radius of the nucleus in the ground state, and $\Delta|\psi_{ns}|^2$ the difference between the electron densities generated by the ns electrons on the nuclei of the absorber and the source of γ-quanta.

Since the change in the population of the valence 5s atomic orbitals (AO) of tin makes the main contribution to $\Delta|\psi_{ns}|^2$, the reason for the interest in the direct estimation of the latter from δ and conversely is fairly obvious.[13,14] However, two difficulties arose in the determination of the above quantities: the lack of an exact value of $\Delta r/r$ and the fairly considerable scatter in the estimates of the shielding influence of the 5s, 5p, and 5d electrons on the 5s electron of the tin atom.[18] The necessity to determine the exact value of $\Delta r/r$ has been discussed in detail.[14] However, hitherto there exists no unanimous view concerning the estimation of $\Delta r/r$, which has been well illustrated in the paper by Vertes et al.[16], where values of $\Delta r/r$ ranging from 0.73×10^{-4} to 2.05×10^{-4} are presented even on the basis of the very latest data.

Allowance for the shielding of the 5s electron by the 5s, 5d, and 5p electrons in the first studies on this question led to different estimates of its extent.[59,60] Subsequently numerous expressions relating the measured values of δ to the population of the 5s, 5p, and 5d AO of tin in compounds were proposed[61-63] but none of them is sufficiently universal.[18] This situation is clearly demonstrated by Table 3, which lists the values of δ for tin species widely used in catalysis–$SnCl_4$ and $SnCl_3^-$; these values were calculated using the populations of the 5s (S) and 5p (P) AO obtained[17,18,64] from the three formulae proposed by Antoncik[61] and also from the formulae quoted by Gol'danskii and Makarov[59] and by Flin.[60] Evidently, within the framework of any of the approximations for the estimation of S and P for the same compound, the values of δ differ by a factor of 1.5–3. At the same time the data in Table 3 show that the parametrisation of the semi-empirical LCAO-MO method yields differences of the same order of magnitude. Whereas calculation for $SnCl_4$ yields as a rule values of δ which are much too high, within the framework of the same LCAO-MO approximation those obtained for $SnCl_3^-$ are too low. Here one must note that the dependences of δ on S, P, and D have been obtained using different values of $\Delta r/r$. Thus Gol'danskii and Makarov[59] adopted 3.3×10^{-4}, while Antoncik[61] adopted 0.92×10^{-4}.

Thus neither the parametrisation of the LCAO-MO methods for tin compounds nor the estimation of the populations of the 5s, 5p, and 5d AO for the tin atom in such compounds on the basis of the measured δ are possible without refining and standardising the values of $\Delta r/r$ and the shielding parameters. However, within the framework of a narrow range of compounds, any of the proposed dependences of δ on S, P, and D reproduce satisfactorily the principal characteristics of the changes in $\Delta|\psi_{5s}|^2$. Thus the populations of the 5s and 5p AO of the tin atom in $SnCl_3^-$ and the complexes obtained in terms of the Mulliken–Wolfsberg–Helmholtz (MWH) approximation[51] yield the following values of δ estimated by the formula quoted by Herber et al.[63]: 3.38 mm s^{-1} for $SnCl_3^-$, 2.8 mm s^{-1} for $[PtCl_3(SnCl_3)]^{2-}$, and 2.96 mm s^{-1} for $[PtCl_2(SnCl_3)_2]^{2-}$. These results show that the MWH approximation can reflect fairly roughly the charge distribution in the complex but the principal features (the decrease of $\Delta|\psi_{5s}|^2$ for the tin atom on coordination and its greatest decrease for the complex with the M:Sn = 1:1 ratio) are reproduced correctly.[51]

Table 3. The parameters δ obtained in calculations of the populations of the 5s and 5p AO of the tin atom in terms of the LCAO-MO approximations.

Method of calculation of S and P	δ*($SnCl_4$)					δ*($SnCl_3^-$)				
	1**–[63]	2–[63]	3–[63]	[59]	[60]	1–[63]	2–[63]	3–[63]	[59]	[60]
CNDO (Ref.64)	1.12	2.2	0.74	1.68	1.95	—	—	—	—	—
CNDO-CI (Refs.17, 18)	2.05	3.44	2.16	2.63	3.03	3.19	5.27	3 31	2.62	4.24
MWH (Ref.18)	0.99	2.1	0.82	1.60	1.80	2.33	2.18	2.40	1.92	2.83

*The parameters δ are given relative to $Ba^{119}SnO_3$: $\delta_e(SnCl_4) = 0.85$ mm s^{-1};[65] $\delta_e(SnCl_3^-) = 3.64$ mm s^{-1}.[28]
**The numerals 1, 2, and 3 refer to the dependences of δ on S and P taken from Ref. 63 (in sequence).

Note. The numerals in square brackets denote references (Ed.of Translation).

Direct correlations between δ_e and $\Delta|\psi_{5s}|^2$ have been used in a number of studies and satisfactory results have been obtained.[16,64,66] They show that, at least in a series of related compounds, it is possible to interpret the differences in δ as a consequence of the changes in the population of the 5s AO of the tin atom. This information is important for the study of the mutual influence of the ligands in the complex and also for the determination of the AO involved in the interaction of the homogeneous catalyst with the molecule being activated and in the change of the properties of the catalyst under various conditions.

In discussing the possibility of using the Mössbauer parameters to characterise the features of the electronic structure of tin halide complexes, it is essential to consider the problem of the use for this purpose of quadrupole splitting in a number of investigations. We have

$$\Delta = \frac{e^2qQ}{2}\left(1+\frac{\eta^2}{3}\right)^{1/2} , \qquad (9)$$

where eq is the electric field gradient (EFG) at the nucleus in the direction of the emission of γ-quanta (the z axis), Q the quadrupole moment of the nucleus characterising the deviation of the distribution of the average charge density on the nucleus from spherical symmetry and $\eta = (q_{xx}-q_{yy})/.q_{zz}$ the asymmetry parameter.[13] The gradient eq is determined for tin mainly by the population of the $5p_z$ AO. The expressions for the dependences of the EFG in the direction of the x, y, and z axes (q_{xx}, q_{yy}, and q_{zz} respectively) in terms of the populations of the p_x, p_y, and p_z AO have been published.[13] Thus Δ can serve as a measure of the uniformity of the population of the $5p_{x,y,z}$ AO of the tin atom and is a parameter sensitive to the structure of the immediate environment of the atom.

The authors of one of the first studies[30] on the Mössbauer spectra of $SnCl_3$-containing complexes explained the increase of Δ on passing from salts of the $SnCl_3^-$ anion to complexes by electron transfer from the metal atom to the π^* orbital of $SnCl_3$, incorporating the $5p_{x,\,y}$ AO of the tin atom with the simultaneous decrease of the number of electrons in the $5p_z$ AO owing to the formation of a σ-bond, which intensifies the non-equivalence of the populations of the p AO of the tin atom. Subsequently the chage in Δ was regarded in certain studies, for example, those of Antonov and co-workers,[67,68] as a direct measure of the π-acceptor properties of the ligand SnX_3 (X = Cl or Br), i.e. a measure of the increase of the population of the $5p_{x,\,y}$ AO of the tin atom in the ligand.

The change in the distribution of electron density in the SnX_3^- anions on σ-donor transfer of the electron pair from the highest occupied MO has been analysed.[17,18,34] The data presented show that such transfer does indeed entail a marked population decrease of the $5p_z$ AO of the tin atom, which induces the appearance of a negative q_{zz}, which increases in absolute magnitude from F- to I-derivatives. According to Yurchenko's estimate,[18] this effect leads to the following increments in Δ for the SnX_3 ligand compared with the SnX_3^- ion: 0.83 mm s^{-1} for SnF_3, 1.43 mm s^{-1} for $SnCl_3$, 1.70 mm s^{-1} for $SnBr_3$, and 2 mm s^{-1} for SnI_3. The changes in Δ in the series of X observed for the SnX_3-containing complexes agree with these estimates, although they are somewhat lower in absolute magnitude.[50,51] This shows that the Δ cannot be used to estimate the π-acceptor properties of the ligands SnX_3 without taking into account the contribution to the changes in the population of the $5p_\sigma$ AO of the tin atom as a consequence of the σ-donor transfer $X_3Sn \rightarrow M$.

The values of δ and Δ for the SnX_3-containing complexes have been published mainly in Refs. 1, 18, 19, 29, and 31–36.

The inverse proportionality between δ and Δ can be usually traced in tin(II) compounds with donor–acceptor bonds.[13] In the case of a purely ionic bond between tin(II) and its environment (the $5s^2 5p^0$ configuration), we should have $\Delta = 0$ and an increase of the population of the $5p$ shell should lead to $\Delta \neq 0$. According to Shpinel's estimate,[13] one unbalanced p electron in the z axis direction should then give rise to $\Delta = 3$ mm s^{-1}. However, for coordinated SnX_3 ligands such a relation between δ and Δ has not been observed, as for the tin compounds mentioned above; this serves as yet another piece of evidence demonstrating the complexity of the redistribution of the population of the $5p_{x,\,y,\,z}$ AO of the tin atom on coordination of the SnX_3 groups.

Thus it is at present impossible to predict beforehand which precise changes in δ and Δ will be undergone by particular tin(II) compounds and the structural identification of the latter can be achieved in only one way—by determining the boundary values and other characteristics of the Mössbauer parameters by studying compounds of different types but with known structures established by X-ray diffraction, which has been partly done in two investigations.[17,18]

2. Heterogeneous Systems

Two applications of tin-containing compounds in heterogeneous catalysis have now arisen: (1) the immobilisation of $SnCl_3$-containing transition metal complexes on the surfaces of carriers;[18] (2) the deposition on the surfaces of carriers of either these complexes or of tin-containing compounds and transition metal compounds (usually platinum) separately with subsequent high-temperature reduction until M–Sn alloys are formed.[3] In both cases a series of specific complications arise in the application of the Mössbauer effect for the identification of tin compounds on the surfaces of carriers and for the characterisation of their state.

Thus it has been shown[69] that some of the tin compounds formed on the $ZnAl_2O_4$ surface are readily oxidised by oxygen, which requires the preparation of the specimens and the recording of the spectra under conditions where access of air can be ruled out. Flat sealed bulbs made of thin molybdenum glass have proved very useful for this purpose.[70] In preparing such bulbs, one must keep their flat sides parallel and the distance between them should ensure an effective thickness of the specimen C_a less than unity.[13] Such cells have been used[26,27,54,69–72] to record the Mössbauer effect in the temperature range 77–300 K.

When $SnCl_3$-containing complexes and other tin(II) compounds, for example $SnCl_2$, are fixed on the carrier, the Mössbauer parameters change appreciably;[26,27,54,73] there is a particularly pronounced alteration of f'. Fig. 4 illustrates the changes in f' for different tin(II) compounds when they are deposited on γ-Al_2O_3.[54,55,73] Since the tin(II) compounds were deposited by impregnating the carrier with their solutions in organic solvents, after the removal of the solvent and drying of the specimen, the tin(II) compounds were present on the specimen surface in the form of molecules linked to specific centres on the carrier.[74] In this case the conclusion reached by Yurchenko et al.[55] that an increase of f' (Fig. 4) implies a strong chemical interaction of the $SnCl_3$ ligands in the complex or of the $SnCl_2$ molecules with the surface as a consequence of the partial hydrolysis of the Sn–Cl bond by the acid OH groups,[55] i.e.

$$\left|-OH + Cl-\overset{Cl}{\underset{Cl}{Sn}}-ML_n \rightarrow \right| -O-\overset{Cl}{\underset{Cl}{Sn}}-ML_n + HCl\ , \qquad (10)$$

can be used to explain the changes in f'.

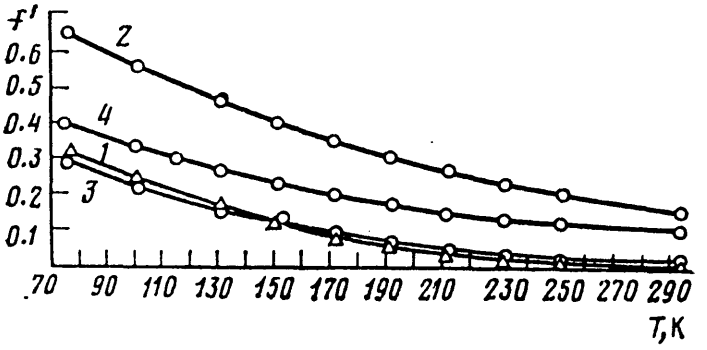


Figure 4. Temperature dependence of f': *1*) $SnCl_2.2H_2O$; *2*) $SnCl_2$ on γ-Al_2O_3; *3*) $(Et_4N)_2[PtCl_2(SnCl_3)_2]$; *4*) $[PtCl_2(SnCl_3)_2]^{2-}$ on the surface of γ-Al_2O_3.

After treating these specimens under the reaction conditions (H_2 atmosphere, temperature 773 K), a set of tin compounds are as a rule formed on the surface, giving rise to very complex overall spectra (Fig. 5, curves *1*, *2*, *5*, and *6*). The identification of individual tin compounds on the catalyst surface requires in such cases the resolution of

the complex contour of the Mössbauer spectrum into individual components. In this case the problem is much more complex than in the analysis of individual Lorentzian components in the spectra of clusters (cf. Fig. 1). Similar complex spectra are observed when different carriers and when different methods of preparation of the catalysts are used.[10,69–72,75–77]

As each of the tin compounds identified can be chemically bound to the surface or can exist in a finely dispersed state, where most of the Mössbauer atoms do not interact with the surface and compounds of this kind do not as a rule exist in an individual state, some uncertainty arises about the selection of the parameters (δ, Δ, and f') of the individual components of the spectrum. Two approaches arose in the consideration of the question of the permissible variation of the Mössbauer parameters of the individual components. In the first, the values of δ and Δ for the individual components remain close to those for the individual substances in the massive state. Clearly such resolution is closer to the true one the coarser the dispersion of the test substances and the weaker their interaction with the surface. If such resolution cannot be carried out, the parameters can be altered somewhat, for example, Δ can be increased, but within the limits of the values encountered for individual systems. The parameter f' is not then measured.[10,70–72]

The second approach consists in the investigation of the changes in δ, Δ, and f' when various tin compounds, whose formation may be expected, interact with the surface, and in the resolution of the overall spectrum into components with parameters corresponding to the interaction of the individual compounds with the surface. It is then implied that the compounds do not interact with one another or that this interaction is not reflected in the Mössbauer

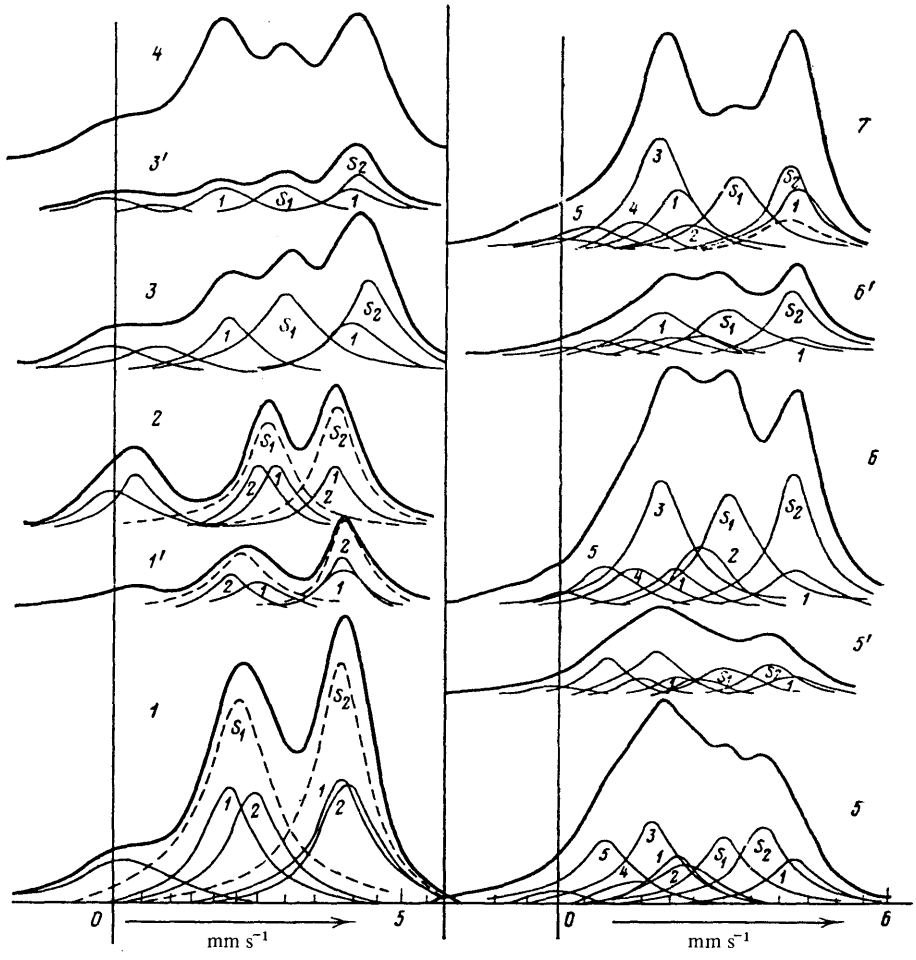


Figure 5. Mössbauer spectra resolved into individual components on an SK-2 synthesiser: *1*) and *1′*) $SnCl_2$ on γ-Al_2O_3; *2*) $SnCl_2$ on γ-Al_2O_3 chlorinated beforehand [γ-Al_2O_3(Cl)]; *3*) and *3′*) specimen 2 reduced in a stream of H_2 (773 K); *4*) overall spectrum of specimen 3 and Pt–Sn alloys; *5*) and *5′*) Pt–Sn/γ-Al_2O_3; *6*), *6′*), and *7*) Pt–Sn/γ-Al_2O_3(Cl); specimens 5 and 6 were obtained by depositing the complex $[PtCl_2(SnCl_3)_2]^{2-}$ and were reduced in a stream of H_2; specimen 7 was obtained after repeated oxidation-reduction cycles; spectra *1*–*7* were recorded at 77 K and spectra *1′*–*6′* at 295 K.

parameters. This approach has been used by Yurchenko and Kuznetsov[73]# and, to a limited extent, without analysis of the values of f', by Gray and Fahra[75] and Berndt et al.[76] However, in this case too it is frequently impossible to achieve a unique resolution and one must consider all the alternative interpretations of the spectra. Such data have been reported.[73,76]

A major complication in the selection of the initial values of δ, Δ, and f' for the resolutions arises from the influence of the degree of dispersion of the compounds on the parameters of the Mössbauer spectra. Analysis of the characteristic features of the Mössbauer spectra of molecular crystals has shown[18,55,73] that the differences between the electronic structures and the dynamics of the movement of the tin atom in a complex molecule are determined predominantly by the molecular structure. Thus the transfer of a molecule from the crystal to the solution hardly influences δ and Δ and entails merely a decrease of f'. The physical adsorption of tin-containing molecules on the carrier surface should therefore not alter δ and Δ either. The observed[26,27,54,73] changes in δ and Δ on deposition of tin compounds on a carrier are in fact associated with the partial alteration of the chemical composition of the molecule, illustrated in Scheme 10, i.e. with the partial replacement of the Cl atom by O in the coordination sphere of tin. One can also assume that tin(IV) compounds (SnO_2, $SnCl_4$, etc.) and tin(II) compounds ($SnCl_2$, $SnCl_2.nH_2O$, SnOHCl, SnO) have (when their molecular composition is retained) values of δ and Δ on the carrier surface close to those characteristic of the individual compounds.

The changes in δ and Δ owing to the possible chemical reactions on the surface can be modelled by investigating the parameters of the spectra of the pure substances analogous to the products of such reactions. The situation is more complex as regards the parameters of the phases with closer packing such as β-tin and Pt–Sn alloys. For example, the study of the dependence of f' on the degree of dispersion of β-tin showed that f' for the surface atoms diminishes markedly.[78] Specimens with particle sizes ranging from 1500 to 200 Å have been investigated,[78] but, from the standpoint of catalysis, even the latter are coarsely dispersed specimens. Information about the changes in f' when the particle size is varied from 200 to 10 Å is essential for catalysis. This problem has not been studied rigorously; the main difficulty in this instance involves the preparation of highly dispersed specimens with a uniform distribution of particles with respect to size.

It follows from general considerations (see, for example, Suzdalev[15]) that the frequency of the phonon spectrum increases for a very small particle size and this can actually lead to an increase of f' for the particles. The transition to clusters (particle size 10–30 Å) should alter not only f' but also the parameters δ and Δ of the Mössbauer atom. Such finely dispersed formations should appear only as a consequence of an intense interaction with the surface and there is no reason to regard them as finely dispersed particles having the properties of the phase present in the coarsely dispersed state. It is more reasonable to regard them as new compounds incorporating carrier atoms in their composition. Such a system (Pt–Sn/SiO_2) has been investigated;[70] the size of particles containing only platinum and tin was 10 ± 3 Å and the Mössbauer effect due to the tin atoms was manifested by a doublet with $\delta = 1.43$ mm s^{-1} and $\Delta = 2.32$ mm s^{-1}.

Thus the final result of the fragmentation of the Pt–Sn alloy particles on the carrier is the formation of clusters, in which the platinum atoms interact with the tin bound to the surface. The parameters δ and Δ of such tin atoms then assume values approaching δ and Δ for the tin(II) complexes with transition metals. At least under the conditions of such dispersion, there is no possibility of a very large increase in Δ, unaccompanied by a significant change in δ, which has been postulated[77] in the resolution of the Mössbauer spectrum of the Pt–Sn/Al_2O_3 catalyst.

A finely dispersed phase of the Pt–Sn alloy, whose parameter δ varies within the limits 1.85–2.13 mm s^{-1} ($\delta = 1.97$ mm s^{-1} for the massive alloy) and Δ varies from 0.3 to 5.26 mm s^{-1}, has been identified[71] on specimens with different platinum contents. The last value should correspond to a difference between the populations of the $5p_\sigma$ and $5p_\pi$ AO of the tin atom of 1.75 electrons. Such a difference has not been observed even for the $SnB_9C_2H_4$ structure, where the coordination of the tin atom models effectively a purely surface disposition on the carrier;[62] it is even more unrealistic for the coordination of the tin atom to the symmetrically arranged electron-saturated Pt(0).[79]

The differences between the permissible variations in δ and Δ, which can be identified on the surfaces of compounds, have been one of the causes of the discrepancies in the descriptions of the state of tin(IV) and tin(II) and of the types of alloys on the surface of γ-Al_2O_3 in the studies of Bacaud and co-workers,[10,77] on the one hand, and Yurchenko and co-workers,[72,73] on the other. In our view, the initial resolution of the spectra for fixed values of δ and Δ for the individual components of the Mössbauer spectrum, corresponding to individual tin compounds, is methodologically correct. When δ and Δ are varied in an arbitrary manner, the resolution ceases to be in any way definite. Simultaneously with this procedure, one should deposit all the necessary individual substances on the carrier, the specimen should be treated under the same conditions as the catalyst, and the variation of δ, Δ, and f' should be investigated, and then the parameters of the individual components obtained on resolution of the spectra of the catalyst should be appropriately corrected. It has been shown[55,73] that in many cases information of decisive importance for the identification of the state of the Mössbauer atom on the surface is provided by the analysis of the temperature variation of f'. The ratio f'_{77}/f'_{295} can be used as the simplest and most convenient parameter of the dependence of f' on T.

In view of the special sensitivity of the parameter f' to the type of the tin-containing compounds, investigation of the specimens at least at 77 and 295 K and the maintanence of the ratios f'_{77}/f'_{295} for all the components on resolution of the spectrum within specific characteristic limits make such resolutions significantly more rigorous as regards the identification of the number and types of different tin-containing formations on the surface. The range of variation of δ and Δ as well as f'_{77}/f'_{295} for the tin compounds identified on the γ-Al_2O_3 surface has been indicated by Yurchenko and Kuznetsov[73]§ and Yurchenko.[18]

The ratios f'_{77}/f'_{295} for different tin(II) and tin(IV) halides, oxides, and sulphides,[80] for massive PtSn and $PtSn_2$ [81,82] alloys, and for SnX_3-containing complexes[55] have been published.

#The analysis of the Mössbauer spectra of such systems is discussed in detail in the paper by V.I.Kuznetsov, A.S.Belyi, and E.N.Yurchenko, J.Catal (in the Press).

§See the previous footnote concerning the report of Yurchenko and Kuznetsov.[73]

III. THE PROPERTIES OF TIN-CONTAINING CATALYSTS

1. Homogeneous Catalysts

Matvienko[1] gave a systematic account of most of the studies published up to 1978 where platinum metal compounds with the $SnCl_3$ ligand have been used as catalysts of the reactions of various organic substances. In the same communication and also in Yurchenko's thesis,[18] it is noted that the state of the $SnCl_3$-containing complexes in the reaction medium has not been established in any of these catalysts. Mössbauer spectroscopy has not been used for such purposes.

Later, several communications, also dealing with the catalytic properties of $SnCl_3$-containing complexes, were published. It has been reported[83] that, in the presence of the complex $Rh(PPh_3)_3.(SnX_3)$ (X = Cl or Br), catalytic hydrogenation of olefins takes place. The authors concluded that an unidentified hydride complex exhibits a hydrogenating activity. It has been found[84] that the rhodium(I) complex $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ is active in the isomerisation of olefins, but it has been concluded[67] that the complex should be regarded as a rhodium(III) compound, apparently having the composition $[RhCl_4(SnCl_3)_2]^{3-}$.[85] Antonov et al.[67] investigated $SnCl_3$-containing rhodium(III) compounds ranging from $[Rh(SnCl_3)_2Cl_4]^{3-}$ to $[Rh(SnCl_3)_5Cl]^{3-}$ (by the Mössbauer method), but their state in the presence of olefins was not characterised. Borunova et al.[86] examined the catalytic properties of the complexes $[MX(SnX_3)_5]^{n-}$ (M = Pt, Rh, Ir, Ru, or Os, X = Cl or Br) in the hydrogenation and isomerisation of olefins. The initial compounds were characterised by Mössbauer spectroscopy mainly in the study of Yurchenko et al.[32] However, in this case the authors concluded that the complex undergoes a change in composition in solution and that hydride forms are active, for example, in isomerisation, but these two were not identified or investigated by Mössbauer spectroscopy either. This applies likewise to the complex $[Ru(PPh_3)_2.(SnCl_3)Cl]$, in the presence of which catalytic hydrogenation of olefins takes place.[87]

Thus only the initial $SnCl_3$-containing complexes, forming the intrinsic catalytically active species under the conditions of the catalysis, have been characterised by the Mössbauer method in the studies enumerated above. The lack of Mössbauer spectroscopic data for the intrinsic catalytically active forms precludes the analysis of the relation between their δ and Δ, on the one hand, and the catalytic activity of such compounds, on the other. This situation can be avoided perhaps only in the case of the chlorocarbonyltin complexes $[IrClCO(SnCl_3)_2]^{2-}$ (I), $[RhClCO(SnCl_3)_2]^{2-}$ (II), $[PtCl_2CO(SnCl_3)]^{-}$ (III), and $[IrCl_3CO(SnCl_3)_2]^{2-}$ (IV), which have been investigated by a series of physical methods, including Mössbauer spectroscopy.[34] It has been shown[1,18] that these complexes are in fact the catalytically active forms in the homogeneous dehydrogenation of HCOOH. In this connection, one may note that for the first three complexes in which the transition metal has the d^8 configuration, the reaction rate constants k, δ, and Δ vary in parallel: 3×10^{-3} s^{-1}, 1.73 mm s^{-1}, and 2.15 mm s^{-1} for compound (I), 1.2×10^{-4} s^{-1}, 1.64 mm s^{-1}, and 1.92 mm s^{-1} for compound (II), and 1.5×10^{-5} s^{-1}, 1.58 mm s^{-1}, and 1.60 mm s^{-1} for compound (III).[1] On passing to the iridium(III) compound with the d^6 configuration, k diminishes appreciably (4.5×10^{-5} s^{-1}), but δ and Δ for the Sn atom in the $SnCl_3$ ligands in this complex increase (1.83 and 2.08 mm s^{-1} respectively).

Thus the direct relation between the Mössbauer parameters and the rate constants for catalytic reactions in such systems can hardly be regarded as adequately universal. Analysis of the mechanism of the catalytic dehydrogenation of HCOOH, proposed by Yurchenko and Anikeenko,[88] and also valid for $SnCl_3$-containing complexes,[1] showed that the properties of this ligand influence two stages of the process: the substitution of one $SnCl_3$ ligand by $HCOO^-$ and the rate-limiting stage involving the rupture of the H—C bond. The role of the intrinsic properties of the ligand in cases where the central atom of the complex is Ir(I) or Ir(III) is indeed found to be different.[18,88]

The first tin-containing zerovalent palladium clusters which have been obtained and characterised[21] proved to be catalytically active in the conversion of olefins into the cyclic esters of polyhydric alcohols (anhydroalditols).[1] In this case Mössbauer study of the clusters made it possible to refine their composition.[21] It was mentioned above why the parameters f' were used for this purpose (Fig. 1). For all the palladium clusters, the values of δ and Δ for the individual Lorentzian components were analysed together with f'. In particular, it was shown that the observed δ for the second type of tin(II)-containing ligand satisfy the condition of a linear decrease of the 5*s* electron density in the sequence $PdSnCl_3 > Pd_2SnCl_2 > Pd_3SnCl > Pd_4Sn$.[21] Anions having the composition $[Pd_2(SnCl_2)_2(SnCl_3)_4]^{2-}$, $[Pd_3(SnCl)_2.(SnCl_3)_6]^{4-}$, and $[Pd_4(Sn)_2(SnCl_3)_8]^{4-}$ have been identified.[1,21] A communication has been published recently[89] whose authors, repeating Matvienko's study,[1] found other compositions of clusters containing four palladium atoms: $[Pd_4(SnCl_2)_2(SnCl_3)_8]^{5-}$ and $[Pd_4(SnCl_2)_2(SnCl_3)_4Cl_2]^{6-}$. The communication[89] contains no arguments justifying this difference nor a discussion of the structure of the clusters obtained. The measured parameters of the Mössbauer spectra of the above compounds, which differ from the parameters quoted for clusters by Elizarova et al.[21], do not prove that Antonov et al.[89] obtained compounds having a composition different from those found by Matvienko[1] because δ and Δ for familiar palladium(II) complexes, in particular $[Pd(SnCl_3)_5]^{3-}$, obtained by Antonov et al.[89] differ from those found in other studies[1,21,33,34] by an amount greatly exceeding the experimental error.

The Mössbauer method occupies a notable place in studies where questions concerning the formation and stability of $SnCl_3$-containing complexes and the mutual influence of the ligands in them, which are important for homogeneous catalysis, are investigated. The formation of such complexes in methanolic and aqueous HCl solution was first investigated by the Mössbauer method in the $H_2PtCl_6.H_2O$–$SnCl_2.2H_2O$ system.[24] The authors observed the reduction of platinum(IV) to platinum(II) by bivalent tin, demonstrated the coordination of the platinum(II) atom to $SnCl_3$, and attempted to determine the composition and stability of the complex formed in solution from saturation curves. Later it was shown[25] that the inflections in the saturation curves for such systems do not yield reliable information about the composition of the complexes formed. In the given study of complex formation in the system comprising K_2PtCl_4 in 0.5 M HCl solution and $SnCl_2.2H_2O$, the composition of the dominant complexes was determined from the characteristic values of δ and Δ for the individual components after the resolution of the spectrum into the Lorentzian doublets. Two complexes with the Pt : Sn = 1 : 2 ratio and a 1 : 5 complex were identified. It was observed that in solution tin(IV) appears rapidly for low Pt : Sn ratios (1 : 1–1 : 2), which might have indicated the reduction of platinum(II) to the zerovalent state with formation of the $[Pt_3Sn_8Cl_{20}]^{4-}$ state.[1]

Yurchenko et al.[26] investigated analogously the formation of complexes between $RuCl_6^{2-}$ and $SnCl_2$ in aqueous 3 M HCl

solution. The composition of the complex was also not determined from the point of inflection in the relation between the concentration of the tin bound in the complex and the Sn : Ru ratio in the system, but was found from the parameters δ and Δ, which were compared with their values for the individual species $[RuCl(SnCl_3)_5]^{4-}$. In view of their identity over the entire range of Sn : Ru ratios, it was concluded that only this complex is formed under the conditions considered.

The complex formation reaction between $IrCl_6^{3-}$ and $SnCl_2$ in aqueous 3 M HCl solution has been investigated by Antonov et al.[90] who obtained the same Mössbauer parameters of the complex $[IrCl(SnCl_3)_5]^{3-}$ as those discussed previously[34] and this finding, and not the Sn : Ir ratios at which inflections were observed on the saturation curves, confirms the validity of the determination of the composition of this complex in solution.

Thus the saturation curves for the formation of complexes of $SnCl_3$ with a transition metal, plotted from data obtained by any of the physical methods, do not constitute a reliable means of determining the composition of the complex and, when Mössbauer spectroscopy is used for this purpose, it is essential to compare the parameters of the differentiated doublets with those of the spectra of the individual compounds. It has been shown[33] that the variation of the nature of the cations in the latter affects to some extent only the magnitude of Δ, which makes it possible to compare δ and Δ *for complex anions in solutions with the corresponding parameters of their salts.* In view of the foregoing, the identification of the complex $[IrCl_4(SnCl_3)_2]^{3-}$ by Antonov et al.[90] appears controversial.

The investigation of the state of the $SnCl_3$-containing complexes in solution was subsequently continued.[21,26,27] Analysis of frozen $PdCl_4^{2-}$ and $SnCl_2$ solutions in methanol and in aqueous 2.4 M HCl solution, after standing for a long time in an inert atmosphere, confirmed that the rapid process involving the formation of palladium(II) complexes with the $SnCl_3$ ligand is accompanied by the reduction of palladium(II) to zerovalent palladium, which forms, at a specific instant, clusters whose composition was discussed above.

The complex formation reaction between H_2PtCl_6 and $SnCl_2$ in aqueous acetone solution containing HCl has been studied[27] and the dynamics of the behaviour of two types of complexes, namely $[PtCl_3(SnCl_3)]^{2-}$ (A) and $[PtCl_2.(SnCl_3)_2]^{2-}$ (B) was followed. It was found that, apart from the reduction of platinum(IV) to platinum(II) and the formation of platinum complexes indicated above, there is a slow increase of the amount of tin(IV) in the system. After a time, the complex (B) was converted into the complex (A) and the platinum in the latter was reduced to the zerovalent state.¶ The formation of a platinum(II) chloride complex with $SnCl_2.2H_2O$ in isopropyl alcohol has been investigated[21] by Mössbauer spectroscopy. Two types of complexes, namely $[Pt(SnCl_3)_5]^{3-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$, were found. Depending on the HCl content, they can be interconverted. The platinum(II) complexes of the first type are stabilised at high HCl concentrations. After a time, the successive transformation $[Pt(SnCl_3)_5]^{3-} \rightarrow [PtCl_2(SnCl_3)_2]^{2-} \rightarrow [PtCl_3.(SnCl_3)]^{2-} \rightarrow$ Pt–Sn alloy takes place. The alloy is present in solution in an ultradispersed state in a mixture with the last two complexes.

Thus Mössbauer studies of the state of the platinum and palladium complexes of the $SnCl_3$ ligand in various solutions revealed their important feature—their tendency towards slow inner-sphere conversion by an oxidation-reduction reaction into clusters of zerovalent metals or into intermetallic compounds.

We shall consider briefly the results of the application of Mössbauer spectroscopy to the study of the mutual influence of ligands. It has been shown[17,34] that a combination of Mössbauer spectroscopy, NMR, RyPES [Rydberg photoelectron spectroscopy?], and, for carbonyl complexes, infrared spectroscopy is useful. The overall results of such studies have shown that the relative σ-donor and π-acceptor capacities of the $SnCl_3$ ligand vary markedly as a function of the nature of the partners in the coordination sphere. Thus, in complexes of the type $PtCl(SnCl_3)L_2$ and $Pt(SnCl_3)_2L_2$ with L = $P(OR)_3$, the $SnCl_3$ *cis*-ligand diminishes competitively with the π-acceptor interaction $M \rightarrow P(OR)_3$. When L = PR_3, the influence of the $SnCl_3$ *cis*-ligand consists in a marked weakening of the σ-donor interaction $R_3P \rightarrow M$. In compounds of the type $[MCl_3CO(SnCl_3)_2]^{2-}$, where M = Rh(III) and Ir(III), the $SnCl_3$ ligands have the same influence on CO and the charge state of M as PR_3 in $MCl_3CO(PR_3)_2$, but in the complex $[MClCO(SnCl_3)_2]^{2-}$ the $SnCl_3$ ligand exhibits more pronounced σ-donor and π-acceptor properties than PPh_3 in $MClCO(PPh_3)_2$, such properties being more marked in the iridium(I) complex than in the rhodium(I) complex.

For this reason, in complexes of various types, the $SnCl_3$ ligand occupies different positions in the series based on the *trans*- or *cis*-influence and, depending on the nature of the other ligands, the influence itself is manifested unequally in the sense of the involvement in it of the σ-donor and π-acceptor interactions of M with $SnCl_3$. As a general characteristic of the mutual influence of ligands in such complexes, one may mention the tendency of $SnCl_3$ to have the minimum number of *trans*-partners L with σ-donor and π-acceptor properties [L = PR_3, $P(OR)_3$, CO, or $SnCl_3$]. *cis*-$SnCl_3$ exerts a dominant influence on the most pronounced properties of the ligand L (σ-donor or π-acceptor).

The influence of the central metal atom M on the state of the ligand $SnCl_3$ in a wide range of compounds cannot be investigated, since they differ significantly in composition and structure. For the complexes $[MX(SnX_3)_5]^{n-}$ and $[M(SnX_3)_5]^{m-}$ (X = Cl or Br), the 5*s*-electron-accepting capacities of d^6 and d^8 metals decrease in the sequences Ir(III) > OS(II) $\geq$ Ru(II) [32] and Pt(II) > Pd(II) > Rh(I) [33] respectively.

2. Heterogeneous Catalysts

As stated above (Section I), the main type of industrial heterogeneous catalytic systems comprises Pt–Sn alloys on various carriers. As mentioned above, apart from the alloys, the surface of the carriers contains also a whole series of tin(II) and tin(IV) compounds, each of which can play a definite role in complex catalytic processes. For example, in the case of catalysts consisting of a solid solution of SnO_2 in MoO_3 on the SiO_2 surface, the Mössbauer spectroscopic method demonstrated that the propene oxidation reaction leads to the formation of an adsorption complex of acroleine and tin(II),[91] which indicates unambiguously the involvement in the reaction of not only molybdenum(VI) compounds but also of tin(IV) and tin(II) compounds.

The results of the study of the Pt–Sn catalysts on various carriers[69–72,75,76] show that the composition of the compounds formed in a reductive medium on the surface is determined by

¶ Unfortunately, as a result of an error by the Publishing House, in the issue of the journal React. Kinet. Catal. Letters containing Refs. 26 and 27, Fig. 1 from Ref. 26 and Fig. 2 from Ref. 27 were transposed. Readers are requested to take this fact into account.

the composition of the deposited compounds and the properties of the carrier.

Mössbauer spectroscopic study of the phase composition of the Pt–Sn/$ZnAl_2O_4$ catalyst at all stages of its preparation as a function of the composition of the solution containing platinum and tin(II) compounds showed that, after deposition on the surface of the zinc–aluminium spinel, the main bulk of tin is present as SnO_2 and in a smaller proportion as the complex containing Pt–$SnCl_3$; when $SnCl_2$ is present in solution in an excess, tin(II) is formed on the surface with $\delta = 3.25$ and $\Delta = 1.85$ mm s^{-1}, indicating a strong interaction with the surface of the tin not bound to platinum.[69,71] In the course of the dehydrogenation of n-butane in a reductive medium, some of the tin(II) (both bound and not bound in the complex) forms alloys with platinum. The alloy composition depends on the Pt:Sn ratio in the complex predominating in the impregnating solution.[18,71] For Pt:Sn ratios of 1:1 and 1:2 in the complex, mainly the Pt_3Sn alloy, which exhibits the highest catalytic activity among all Pt–Sn alloys and ensures a fairly high stability of the catalyst, is formed preferentially on $ZnAl_2O_4$.[18,71] The ratio f'_{77}/f'_{293} for SnO_2 in such a catalyst is 7.7, which is appreciably higher than the corresponding parameter for massive SnO_2 and can indicate a high degree of dispersion of the particles on the carrier surface. The Mössbauer parameters of the alloys are close to those for the massive specimens, which was explained by the lower degree of dispersion of the particles of the Pt–Sn alloys compared with the state of SnO_2.[18]

Taking into account the values of f' for the individual components of a similar catalyst, the kinetics of the formation of specific tin compounds on the surface have been investigated[75] by the Mössbauer method and a mechanism has been proposed for the oxidative dehydrogenation of paraffins. In the above study data were obtained for the first time demonstrating the strong interaction of part of the tin(II) with the carrier surface, leading to the formation of $SnAl_2O_4$.

When tin(II) and platinum(II) compounds with organic ligands were deposited on the SiO_2 surface with subsequent reduction, the formation of $SnSiO_3$ was observed by the Mössbauer method, which can also be regarded as a result of the insertion of tin(II) in the SiO_2 lattice with its subsequent partial reorganisation.[70] A detailed study has been made[76] of the genesis of the phase composition of the Pt–Sn catalyst on the η-Al_2O_3 carrier. A strong interaction of tin(II) with the surface was also observed and it was shown that the deposition of platinum(II) and tin(II) on the carrier in the form of an $SnCl_3$-containing platinum complex leads to their more intense interaction in the catalyst than in the case where the chlorides $PtCl_4^{2-}$ and $SnCl_4$ are deposited separately. It was found that the parameter δ for the alloys decreases linearly with increase of their platinum content and that the activity in dehydrocyclisation is associated with the modification of the properties of platinum atoms by tin.

The methodological problems arising in the analysis of the complex Mössbauer spectra of such catalysts were discussed above. In this connection the details of the identification of the types of compounds in the Pt–Sn catalyst deposited on γ-Al_2O_3, quoted by Bacaud and Bussiere,[77] must be treated critically. However, it is true that, as in catalysts incorporating other carriers, on the γ-Al_2O_3 surface there are several states of the tin(IV) and tin(II) atoms and several types of Pt–Sn alloys. This is also confirmed by the Mössbauer spectra of the Pt–Sn/γ-Al_2O_3 systems[18,73] resolved into the individual Lorentzian components by the second method (see above), which are illustrated in Fig. 5 (spectrum 5). Two states of tin(IV) [one close to SnO_2 and the other close to $SnCl_4$ and giving rise to a singlet (curve 5); both states interact with the carrier], two states of tin(II) [$SnAl_2O_4$ giving rise to a doublet (curve *1*) and $SnCl_2$ interacting with oxygen on the surface via Scheme (10) and giving rise to an S_1–S_2 doublet], and a series of Pt–Sn alloys (Pt_3Sn, singlet *4*; PtSn, singlet *3*; $PtSn_4$, singlet *2*) have been identified on the surface of this catalyst.[18]

Pt–Sn reforming catalysts, obtained by depositing $SnCl_3$-containing platinum complexes on γ-Al_2O_3 chlorinated beforehand [γ-Al_2O_3(Cl)] have been investigated by the Mössbauer method.[18,72,73] The Mössbauer spectra were analysed by Kuznetsov et al.[72] using the first resolution procedure and by Yurchenko[18] and Kuznetsov[73] using the second procedure (see above), according to which a preliminary study was made of the interaction of $SnCl_2$ with γ-Al_2O_3 and γ-Al_2O_3(Cl) during the preparation of the catalyst (Fig. 5, curves *1–4*). It was shown that prolonged treatment of the catalyst under conditions close to those during catalysis alters appreciably the quantitative composition of the tin-containing components (cf. spectra *6* and *7* in Fig. 5) and intensifies the interaction of part of tin(II) and Al_2O_3(Cl) with formation of tin(II) having δ close to that of anhydrous $SnCl_2$ (the singlet shown dashed in spectrum *7* in Fig. 5). More detailed characteristics of the state of tin(II) not bound to platinum on the surface were obtained by using for this purpose the temperature dependence of the parameter f',[18,73] the extent of which can be deduced by comparing the Mössbauer spectra in Fig. 5 at 77 K (spectra *1–7*) and 293 K (spectra *1′–7′*). Otherwise, the two methods of analysis of the Mössbauer spectra yielded similar results not only as regards the identification of the principal tin containing components of the catalyst (cf. spectra 5 and 6 with Fig. 1 in Ref. 72) but also as regards their amounts on the surface.[18,73] It has been shown[18,72,73] that the modification of the carrier by introducing Cl atoms into the latter entails a significant change in the state of the tin(II) compounds in the catalyst.

The fundamental difference between the carriers based on γ-Al_2O_3 and $ZnAl_2O_4$ is that the former ensures a more ready susceptibility of tin(IV) to reduction and stabilises the state of tin(II) in tin-containing components of the catalyst.[18,72]

Thus the composition of the catalyst might have differed appreciably in different investigations as a consequence of the differences in the methods used to deposit platinum and tin, the conditions in the preliminary preparation of the Al_2O_3 surface, and, mainly, owing to the different nature of the carrier itself: γ-Al_2O_3,[10,72,73,76] η-Al_2O_3,[76] Zn–Al spinel,[69,71,75] and SiO_2;[70] they might also have differed owing to the differences between the procedures used in the analysis of the complex Mössbauer spectra of such systems discussed above.

Apart from the Pt–Sn alloys on carriers, which catalyse processes at high temperatures, the possibilities of the immobilised $SnCl_3$-containing complexes as heterogeneous catalysts of low-temperature processes have been attracting increasing attention recently. The first steps on these lines have already been taken. Thus it has been shown[85] that $[RhCl_4(SnCl_3)_2]^{3-}$ fixed on an anion-exchange resin catalyses the dimerisation of ethylene at 50–70 °C but the states of the complex on the anion exchanger and after exposure to the reaction conditions have not been investigated by the Mössbauer method. It has been shown[18] that carbonyltin halide complexes, which are active in the homogeneous-catalytic dehydrogenation of HCOOH (see Section III), can be immobilised on the γ-Al_2O_3 and SiO_2 carriers without loss of their catalytic properties. The Mössbauer parameters of the immobilised complexes indicate the interaction of a proportion of their $SnCl_3$ ligands via Scheme 10 with the surface OH groups; for example, such interaction of the complex [$PtCl_2$.

$.(SnCl_3)_2]^{2-}$ entails a change of δ from 1.64 to 1.52 mm s^{-1} and of Δ from 2.11 to 2.2 mm s^{-1}; f' increases and its temperature variation becomes less marked (Fig. 4). The Mössbauer parameters of the carbonyltin chloride complexes enumerated vary analogously.

IV. CONCLUSION

Extensive information has thus been accumulated about the Mössbauer effect involving the ^{119}Sn(II, O) nuclei in various tin halide complexes, clusters, and intermetallic compounds. Tin(IV) compounds, including organotin compounds, have been studied even more vigorously.[11] All these data have created a basis for a wider-scale employment of the Mössbauer method in the study of the structure and properties of various homogeneous and heterogeneous tin-containing catalysts.

The lack of exact values of f' and of their temperature variation for many individual compounds and (especially) for the products of the interaction with the carrier constitutes a major problem, which has inhibited extensive quantitative studies of tin-containing catalysts by the Mössbauer method. It would be useful to obtain general quantitative relations between f' and the parameters characterising the degree of interaction of tin-containing molecules with the carrier surfaces, particularly the relations for the corresponding equilibrium constants and force constants of the adsorbent–adsorbate bonds, using additional information from their vibrational spectra. Studies of the temperature dependence of f' at lower temperatures, down to the temperature of liquid helium, are essential. In general, whereas the parameters δ, Δ, and Γ have been used fairly widely in the study of the state of tin-containing catalytic systems, the parameter f' has not as yet become a widely used means for the investigation of the properties of real catalysts. However, modern technology and the need to develop precise methods for the investigation of the state of heterogeneous M–Sn catalysts will probably correct this situation in the immediate future.

Finally, the greatest problem in heterogeneous catalysis is that of the development of methods for the investigation of the properties of the surfaces of real catalysts. The Mössbauer effect could, in principle, become a basis for such a method. However, a recent international conference on the application of the Mössbauer effect (Alma-Ata, 1983) demonstrated that so far the different versions of the method make it possible to investigate a surface layer which is not less than tens and even hundreds of angstroms thick, whereas for catalysis one requires information about the state of the Mössbauer atoms and the depth equivalent to several monolayers, i.e. up to 10 Å. Presumably Mössbauer spectroscopy, which is already a unique method for the investigation of the state and properties of homogeneous and heterogeneous catalysts containing Mössbauer atoms, will in future occupy a leading position in the study of such systems.

REFERENCES

1. L.G.Matvienko, Candidate's Thesis in Chemical Sciences, Institute of Catalysis, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1978.
2. E.I.Gil'debrand, Symposium, "Geterogennyi Kataliz" (Heterogeneous Catalysis), Izd.Nauka, Alma-Ata, 1975, Vol.14, p.145.
3. G.R.Kotel'nikov, L.V.Strunnikova, V.A.Potapov, and I.P.Arapov, "Katalizatory Degidrirovaniya, Nizshikh Parafinovykh, Olefinovykh, i Alkilaromaticheskikh Uglevodorodov" (Catalysts for the Dehydrogenation of the Lowest Paraffinic, Olefinic, and Alkyl-Substituted Aromatic Hydrocarbons), Izd. TsNIITEneftkhim, Moscow, 1978.
4. V.I.Gol'danskii, Uspekhi Fiz.Nauk, 1966, **89**, 333.
5. V.I.Gol'danskii and I.P.Suzdalev, Uspekhi Khim., 1970, **39**, 1307 [Russ.Chem.Rev., 1970(7)].
6. L.V.Skalkina, I.P.Suzdalev, I.K.Kolchin, and L.Ya.Margolis, Kinetika i Kataliz, 1969, **10**, 456.
7. J.A.Dumesic and H.Topsoe, Adv.Catalysis, 1977, **26**, 121.
8. W.Jones, Symposium, "Characterisation of Catalysts" (Edited by J.M.Thomas and R.M.Lambert) (Translated into Russian), Izd.Mir, Moscow, 1983, p.126.
9. J.G.Stevens, H.M.Calis, and L.H.Bowen, Analyt. Chem.(R), 1982, **54**, 204.
10. R.Bacaud, P.Bussiere, F.Figueras, and J.P.Mathieu, Compt.rend., 1975, **281C**, 159.
11. P.Bussiere, Rev.Phys.Appl., 1984, **16**, 447.
12. G.K.Wertheim, "The Mössbauer Effect: Principles and Applications" (Translated into Russian), Izd. Mir, Moscow, 1966, p.172.
13. V.S.Shpinel', "Rezonans Gamma-Luchei v Kristallakh" (The Gamma-Ray Resonance in Crystals), Izd. Nauka, Moscow, 1969, p.407.
14. "Chemical Applications of Mössbauer Spectroscopy" (Russian translation from English edited by V.I.Gol'danskii, L.I.Krizhanskii, and V.V.Khrapov), Izd.Mir, Moscow, 1970.
15. I.P.Suzdalev, "Dinamicheskie Effekty v Gamma-Rezonansnoi Spektroskopii (Dynamic Effects in Mössbauer Spectroscopy), Atomizdat, Moscow, 1979.
16. A.Vertes, L.Korecz, and K.Burger, "Mössbauer Spectroscopy", Akademai Kiado, Budapest, 1979.
17. E.N.Yurchenko, V.I.Kuznetsov, and L.Ya.Al't, Zhur.Strukt.Khim., 1982, **23**, 63.
18. E.N.Yurchenko, Doctoral Thesis in Chemical Sciences, Institute of Inorganic Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1985.
19. T.S.Khodasheva, V.A.Varnek, E.N.Yurchenko, and M.A.Porai-Koshits, Dokl.Akad.Nauk SSSR, 1975, **224**, 1323.
20. V.A.Varnet and E.N.Yurchenko, Teor.Eksper.Khim., 1975, **11**, 700.
21. G.L.Elizarova, L.G.Matvienko, E.N.Yurchenko, and R.N.Stukova, Koord.Khim., 1980, **6**, 1731.
22. V.A.Varnek, Pribory i Tekh.Eksper., 1978(4), 79.
23. E.V.Kapitanov and E.N.Yakovlev, J.Phys.C, 1980, **13**, 3435.
24. G.V.Novikov, V.A.Trukhanov, A.P.Khrushch, A.E.Shilov, and V.I.Gol'danskii, Dokl.Akad.Nauk SSSR, 1969, **189**, 1294.
25. E.N.Yurchenko, V.A.Varnek, L.G.Matvienko, and G.L.Elizarova, Koord.Khim., 1977, **3**, 588.
26. E.N.Yurchenko, V.I.Kuznetsov, V.P.Melnikova, and A.N.Startsev, React.Kinet.Catal.Letters, 1983, **23**, 137.
27. E.N.Yurchenko and V.I.Kuznetsov, React.Kinet. Catal.Letters, 1983, **23**, 113.
28. J.D.Donaldson, D.C.Puxley, and M.J.Tricker, J.Inorg.Nucl.Chem., 1975, **37**, 655.
29. D.E.Fenton and J.J.Zuckerman, Inorg.Chem., 1969, **8**, 1771.

30. V.I.Baranovskii, V.P.Sergeev, and B.E.Dzevitskii, Dokl.Akad.Nauk SSSR, 1969, **184**, 632.
31. G.L.Elizarova, E.N.Yurchenko, V.A.Varnek, V.K.Sokolova, and L.G.Matvienko, Zhur.Neorg. Khim., 1974, **19**, 454 [Russ.J.Inorg.Chem., 1974(2)].
32. E.N.Yurchenko, P.G.Antonov, V.A.Varnek, V.I.Konnov, A.I.Shan'ko, and Yu.N.Kukushkin, Koord.Khim., 1976, **2**, 1632.
33. V.A.Varnek, E.N.Yurchenko, G.L.Elizarova, A.I.Shan'ko, L.G.Matvienko, P.G.Antonov, and Yu.N.Kukushkin, Koord.Khim., 1975, **1**, 161.
34. E.N.Yurchenko, V.A.Varnek, G.L.Elizarova, L.G.Matvienko, and M.S.Ioffe, Koord.Khim., 1975, **1**, 1406.
35. E.N.Yurchenko, "Proceedings of the VIth Conference on Coordination Chemistry. Smolenice-Bratislava", 1975, p.309.
36. E.N.Yurchenko, E.T.Devyatkina, T.S.Khodasheva, M.A.Porai-Koshits, V.I.Kontsov, V.A.Varnek, P.G.Antonov, and Yu.N.Kukushkin, Koord.Khim., 1979, **5**, 552.
37. Yu.Kagan and V.A.Maslov, Zhur.Eksper.Teor.Fiz., 1961, **1**, 1296.
38. Yu.Kagan and Ya.Iosilevskii, Zhur.Eksper.Teor.Fiz., 1963, **44**, 284.
39. R.A.Stukan, S.P.Gubin, A.N.Nesmeyanov, and V.I.Gol'danskii, Teor.Eksper.Khim., 1966, **2**, 805.
40. U.Gonser, J.Phys.Chem., 1962, **66**, 564.
41. A.Rein and R.H.Herber, J.Chem.Phys., 1975, **63**, 1021.
42. R.H.Herber and M.F.Leahy, J.Chem.Phys., 1977, **67**, 2718.
43. R.H.Herber and A.E.Smelkinson, Inorg.Chem., 1977, **16**, 953.
44. R.H.Herber and M.F.Leahy, Adv.in Chemistry, ser.No.157, Organotin Compounds. New Chemistry and Applications, 1976(10), 155.
45. R.H.Herber, A.E.Smelkinson, M.J.Sienko, and L.F.Schneemeyer, J.Chem.Phys., 1978, **68**, 3705.
46. K.V.Shaitan and A.B.Rubin, Mol.Biol., 1980, **14**, 1323.
47. K.V.Shaitan, A.B.Rubin, D.S.Chernavskii, and A.A.Kilyachkov, Biofizika, 1981, **26**, 228.
48. V.A.Bryukhanov, V.I.Gol'danskii, N.I.Delyagin, A.A.Korytko, E.F.Makarov, I.P.Suzdalev, and V.S.Shpinel', Zhur.Eksper.Teor.Fiz., 1961, **43**, 448.
49. T.S.Khodasheva, M.A.Porai-Koshits, V.P.Nikolaev, and V.N.Shurkina, Zhur.Strukt.Khim., 1980, **21**, 123.
50. E.N.Yurchenko, T.S.Khodasheva, M.A.Porei-Koshits, and V.P.Nikolaev, Koord.Khim., 1980, **6**, 1290.
51. E.N.Yurchenko, T.S.Khodasheva, M.A.Porai-Koshits, V.P.Mel'nikova, and V.F.Brattsev, Koord.Khim., 1985, **11**, 359.
52. J.H.Nelson and N.W.Alcock, Inorg.Chem., 1982, **21**, 1196.
53. L.J.Farrugia, B.R.James, C.R.Lassigne, and E.Wells, Canad.J.Chem., 1982, **60**, 1304.
54. V.I.Kuznetsov and E.N.Yurchenko, "Tezisy Dokladov Mezhdunarodnoi Konferentsii po Primeneniyu Effekta Messbauera" (Abstracts of Reports at the International Conference on the Applications of the Mössbauer Effect), Izd.Nauka Kazakh SSR, Alma-Ata, 1983, 497.
55. E.N.Yurchenko, V.I.Kuznetsov, and E.B.Burgina, Teor.Eksper.Khim., 1985(2), 194.
56. I.P.Suzdalev, V.I.Gol'danskii, E.F.Makarov, A.S.Plachinda, and L.A.Korytko, Zhur.Eksper. Teor.Fiz., 1965, **46**, 1424.
57. E.N.Yurchenko, E.B.Burgina, E.T.Devyatkina, and V.I.Smirnov, Zhur.Prikl.Spektrosk., 1976, **25**, 702.
58. G.L.Yelizarova, L.G.Matvienko, E.N.Yurchenko, V.P.Tretyakov, and V.M.Mastikin, React.Kinet. Catal.Letters, 1975, **2**, 349.
59. V.I.Gol'danskii and E.F.Makarov, Teor.Eksper. Khim., 1967, **3**, 653.
60. P.A.Flin, in "Mössbauer Isomer Shifts", North-Holland Publ., Amsterdam, 1978, p.598.
61. E.Antoncik, Phys.Stat.Sol.(b), 1977, **79**, 605.
62. V.A.Varnek, S.Ya.Dvurechenskaya, V.V.Volkov, and L.N.Mazalov, Zhur.Strukt.Khim., 1980, **21**, 185.
63. R.H.Herber, F.J.Disalvo, and R.B.Frankel, Inorg. Chem., 1980, 1480.
64. N.N.Greenwood, P.G.Perkins, and D.H.Wall, Symp. Faraday Soc. The Mössbauer Effect, 1967(1), 51.
65. N.N.Greenwood and T.C.Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London, 1971.
66. M.L.Unland and J.H.Letcher, J.Chem.Phys., 1968, **49**, 2706.
67. P.G.Antonov, Yu.N.Kukushkin, V.I.Anufriev, L.N.Vasil'ev, and L.V.Konovalov, Zhur.Neorg. Khim., 1979, **24**, 419 [Russ.J.Inorg.Chem., 1979(2)].
68. P.G.Antonov, Yu.N.Kukushkin, L.N.Mitronina, L.N.Vasil'ev, and V.P.Sass, Zhur.Neorg.Khim., 1979, **24**, 1008 [Russ.J.Inorg.Chem., 1979(4)].
69. N.A.Pakhomov, R.A.Bujanov, E.M.Moroz, E.N.Yurchenko, A.P.Chernyshev, N.A.Zaitseva, and G.R.Kotelnikov, React.Kinet.Catal.Letters, 1980, **14**, 329.
70. A.P.Shepelin, A.P.Chernyshev, V.I.Koval'chuk, P.A.Zhdan, E.N.Yurchenko, B.N.Kuznetsov, and Yu.I.Ermakov, Kinetika i Kataliz, 1981, **22**, 716.
71. N.A.Pakhomov, R.A.Byuanov, E.N.Yurchenko, A.P.Chernyshev, G.R.Kotel'nikov, E.M.Moroz, N.A.Zaitseva, and V.A.Potapov, Kinetika i Kataliz, 1981, **22**, 488.
72. V.I.Kuznetsov, E.N.Yurchenko, A.S.Belyi, E.V.Zatolokina, M.A.Smolikov, and V.K.Duplyakin, React.Kinet.Catal.Letters, 1982, **21**, 419.
73. E.N.Yurchenko and V.I.Kuznetsov, "Tezisy Dokladov Mezhdunarodnoi Konferentsii po Primeneniyu Effekta Messbauera" (Abstracts of Reports at the International Conference on the Applications of the Mössbauer Effect), Izd.Nauka Kazakh SSR, Alma-Ata, 1983, p.522.
74. E.A.Paukshtis and E.N.Yurchenko, Uspekhi Khim., 1983, **42**, 426 [Russ.Chem.Rev., 1983(3)].
75. P.R.Gray and F.E.Fahra, "Mössbauer Effect Methodology", Plenum Press, New York, 1976, vol.10, p.47.
76. H.Berndt, H.Mehner, J.Völter, and W.Meisel, Z.anorg.Chem., 1977, **429**, 47.
77. R.Bacaud and P.Bussiere, J.Catal., 1981, **69**, 399.
78. I.P.Suzdalev, M.Ya.Gen, V.I.Gol'danskii, and E.F.Makarov, Zhur.Eksper.Teor.Fiz., 1966, **51**, 118.
79. W.B.Pearsch, "The Crystal Chemistry and Physics of Metals and Alloys", Pergamon Press, New York, 1972.
80. V.A.Bryukhanov, N.N.Delyagin, A.A.Opalenko, and V.S.Shpinel', Zhur.Eksper.Teor.Fiz., 1962, **43**, 432.
81. V.A.Bryukhanov, N.N.Delyagin, R.N.Kuz'min, and V.S.Shpinel', Zhur.Eksper.Teor.Fiz., 1964, **46**, 1996.
82. N.S.Ibragimov, R.N.Kuz'min, and G.S.Zhdanov, Zhur.Eksper.Teor.Fiz., 1965, **49**, 1389.

83. N.V.Borunova, L.Kh.Freidlin, P.G.Antonov, Yu.N.Kukushkin, N.Ya.Trink, V.M.Ignatov, and A.R.Ganeeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, **9**, 2045.
84. L.Kh.Freidlin and N.V.Borunova, Neftekhimiya, 1975, **16**, 508.
85. P.G.Antonov, N.V.Borunova, V.I.Anufriev, and V.M.Ignatov, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., 1979, 952.
86. N.V.Borunova, P.G.Antonov, Yu.N.Kukushkin, L.Kh.Freidlin, N.D.Trink, V.M.Ignatov, and I.K.Shirshinova, Zhur.Obshch.Khim., 1980, **50**, 1862.
87. P.G.Antonov, N.V.Borunova, Yu.N.Kukushkin, and L.Kh.Freidlin, Izv.Vys.Ucheb.Zaved., Khim.i Khim., Tekhnol., 1981, 663.
88. E.N.Yurchenko and N.P.Anikeenko, React.Kinet. Catal.Letters, 1975, **2**, 65.
89. P.G.Antonov, Yu.N.Kukushkin, R.Kh.Krymova, V.G.Shtrin, and Yu.P.Kostikov, Zhur.Obshch. Khim., 1983, **53**, 858.
90. P.G.Antonov, Yu.N.Kukushkin, V.F.Shkredov, and L.N.Vasil'ev, Zhur.Obshch.Khim., 1979, **5**, 561.
91. A.A.Firsova, N.N.Khovanskaya, A.D.Tsyganova, I.P.Suzdalev, and L.Ya.Margolis, Kinetika i Kataliz, 1971, **12**, 792.

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