

# Quenching of the Phosphorescence of Some Chromium(III) Complexes by Molecular Oxygen

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**Abstract:** The quenching of the phosphorescence of a variety of Cr(III) complexes by molecular oxygen was studied in a fluid solvent at different temperatures. No quenching (within experimental error) was observed for complexes with ligands like ethylenediamine ("insulators"), whereas large quenching constants were obtained for complexes with ligands possessing extensive  $\pi$ -electron systems ("conductors"). The activation energy of the quenching reaction and that for solvent fluidity were found to be the same. Only for  $[\text{Cr}(\text{acac})_3]$  was the observed quenching rate constant as large as the maximum rate calculated for a diffusion-controlled reaction.

Molecular oxygen is known to efficiently quench the long-lived phosphorescence of organic molecules either physically or chemically.<sup>1</sup> Recently attention has been focused on this process by new theoretical<sup>2,2</sup> and experimental studies.<sup>4-6</sup> It appears that physical quenching proceeds by energy transfer with a rate which depends on the triplet energy of the donor<sup>7</sup> and, in solution, on the viscosity of the solvent.<sup>1,8</sup>

At low temperature most Cr(III) complexes emit phosphorescence with a lifetime comparable to that of organic molecules,<sup>9,10</sup> and quenching by oxygen in non-degassed solvents must be suspected. However, unlike organic molecules, the Cr(III) ion is shielded by a ligand sphere and the influence of the ligands on the quenching process has to be considered. Since the energy of the <sup>3</sup>E level from which phosphorescence originates changes only slightly with ligand field, it should be possible to study the effect of structure on the quenching process simply by varying the ligand.

In this work measurements are described of the quenching of phosphorescence of some Cr(III) complexes by oxygen. Preliminary studies of Forster and coworkers,<sup>11,12</sup> where no quenching was observed, are extended to a variety of Cr(III) complexes and different temperatures using an apparatus of higher sensitivity and time resolution. Although only a small number of selected compounds were examined, the results are expected to be similar for complexes not included in this choice.

## Experimental Section

Most of the complexes were obtained commercially:  $\text{K}_3[\text{Cr}(\text{CN})_6]$  from City Chemical Corp., New York, N. Y.;  $\text{K}_3[\text{Cr}(\text{NCS})_6]$  and

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$[\text{Cr}(\text{acac})_3]$  (acac = acetylacetonate) both from Alfa Inorganics; *trans*- $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$  was synthesized by cation exchange from the ammonium salt which was purchased from Fisher Scientific Co.  $[\text{Cr}(\text{en})_3](\text{ClO}_4)_3$  (en = ethylenediamine) and  $[\text{Cr}(\text{tn})_3](\text{ClO}_4)_3$  (tn = trimethylenediamine) were prepared by published methods.<sup>13,14</sup> The complexes were recrystallized several times before use from water (en, tn,  $\text{CN}^-$ ), alcohol ( $\text{NCS}^-$ , Reineckate), or benzene (acac).

The complexes were sufficiently soluble for study in a solvent mixture consisting of two parts (per volume) of methanol (Eastman Kodak, reagent grade), one part of ethylene glycol (Eastman Kodak, reagent grade), and one part of distilled water. This solvent forms a clear glass below  $-110^\circ$  and stays clear when warmed to room temperature. The concentrations of the complexes were  $5 \times 10^{-2} M$ , except for  $[\text{Cr}(\text{tn})_3](\text{ClO}_4)_3$  and  $[\text{Cr}(\text{acac})_3]$ , which were  $3 \times 10^{-2}$  and  $2 \times 10^{-2} M$ , respectively. Oxygen was removed by purging the solutions at room temperature with a stream of pure nitrogen (Canadian Liquid Air Co., L grade) which had been passed through a train of washing bottles containing vanadium(II) chloride.

By saturating the solvent with air or pure oxygen (Matheson research grade) at room temperature or at  $0^\circ$ , different reproducible oxygen concentrations could be obtained. The concentrations were determined by chemical analysis.<sup>15</sup>

Quenching of the phosphorescence was studied by lifetime measurements. The apparatus consisted of a condensed flash lamp dissipating about 5 J with a half-peak width of approximately 200 nsec.<sup>16</sup> The light pulse, filtered by a 3-cm layer of a concentrated aqueous solution of  $\text{CuSO}_4$ , was focused on the sample contained in a metal dewar whose temperature was variable from  $-180^\circ$  to room temperature. The sample was cooled by conduction. The emission was collected by a short focal length lens inside the dewar and passed through a filter system consisting of a 2-cm layer of a concentrated aqueous solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , a red filter, and a Bausch and Lomb monochromator. With this arrangement no scattered light was detectable. The decay was recorded with a cooled Philips 150CVP (S1 response) photomultiplier, displayed on a Tektronix 543B oscilloscope and photographed. The decay curves were analyzed by the least-squares method and were found to be exponential.

The temperature was monitored *in situ* by a copper-constantan thermocouple sealed into the Pyrex cell. By this arrangement the thermocouple was kept in a fixed position close to the irradiated part of the sample. Lifetime measurements at different temperatures of the degassed and the air-saturated sample were always carried out in the same cell.

## Results

The phosphorescence lifetimes of the complexes determined in both the air-saturated and deoxygenated solvent in the temperature range from  $-150$  up to  $0^\circ$

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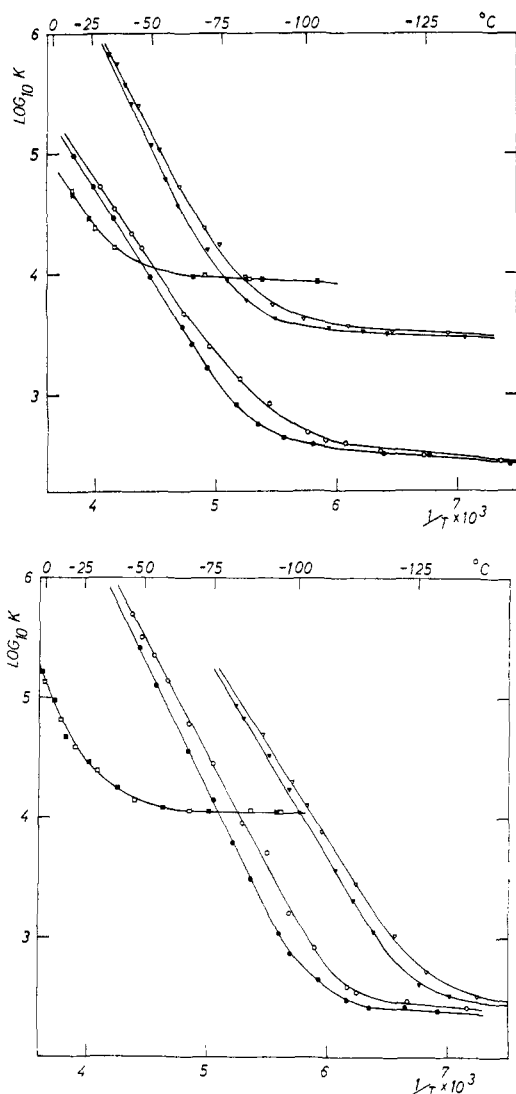


Figure 1. Reciprocal lifetimes as a function of temperature in methanol, water, and ethylene glycol (2:1:1) solvent of (a)  $K[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ,  $\nabla$ ;  $[\text{Cr}(\text{tn})_3](\text{ClO}_4)_3$ ,  $\square$ ; and  $K_3[\text{Cr}(\text{CN})_6]$ ,  $\circ$ ; (b)  $[\text{Cr}(\text{acac})_3]$ ,  $\nabla$ ;  $[\text{Cr}(\text{en})_3](\text{ClO}_4)_3$ ,  $\square$ ; and  $K_3[\text{Cr}(\text{NCS})_6]$ ,  $\circ$  (filled symbols deoxygenated, open symbols air-saturated solutions); [complex] =  $5 \times 10^{-2} M$ , except for  $[\text{Cr}(\text{acac})_3]$  ( $2 \times 10^{-2} M$ ) and  $[\text{Cr}(\text{tn})_3](\text{ClO}_4)_3$  ( $3 \times 10^{-2} M$ ).

are displayed in Figure 1. The lifetime of a  $5 \times 10^{-2} M$   $K_3[\text{Cr}(\text{NCS})_6]$  solution was studied as a function of oxygen concentration at  $-75^\circ$  with the results shown in Figure 2. The phosphorescence lifetime of the deoxygenated solution is  $72.5 \times 10^{-6}$  sec at this temperature.

Preliminary measurements of emission quantum yields of  $K_3[\text{Cr}(\text{NCS})_6]$  and  $K_3[\text{Cr}(\text{CN})_6]$  at  $-75^\circ$  and of photoaquation yields of  $K[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$  at  $-65^\circ$  were also made in the same solvent. In each case a smaller yield was observed when oxygen was present.

The oxygen concentration of the solvent saturated with air at  $25^\circ$  is  $4.5 \times 10^{-4} M$  and it increases to  $5.5 \times 10^{-4} M$  when the solvent is saturated at  $0^\circ$ . The corresponding values for saturation with pure oxygen at 1 atm of pressure are  $16.9 \times 10^{-4}$  and  $18.2 \times 10^{-4} M$ , respectively.

The viscosity of the solvent was found to be  $2.3 \times 10^{-2}$  P determined with an Ostwald-type viscometer at  $25^\circ$ . From viscosity measurements at 0 and  $-76^\circ$  the

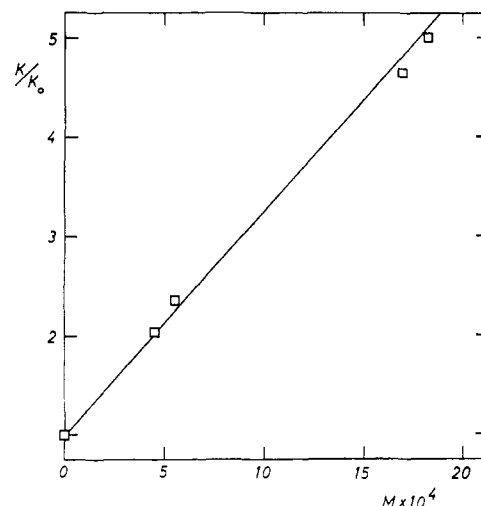


Figure 2. Stern-Volmer quenching of phosphorescence of  $K_3[\text{Cr}(\text{NCS})_6]$  at  $-75^\circ$  in methanol, water, and ethylene glycol (2:1:1) solvent, [complex] =  $5 \times 10^{-2} M$ .

activation energy of solvent fluidity was estimated to be  $6 \pm 1 \text{ kcal mol}^{-1}$ .

### Discussion

A Stern-Volmer mechanism for the quenching of phosphorescence of  $[\text{Cr}(\text{NCS})_6]^{3-}$  by oxygen at  $-75^\circ$  is confirmed by the linear plot in Figure 2. The same mechanism is assumed to apply at other temperatures and for other complexes. The quenching constants were therefore calculated from the equation

$$k_q = [(1/\tau) - (1/\tau_0)]/[\text{O}_2]^{-1} \quad (1)$$

in which  $\tau$  and  $\tau_0$  are the lifetimes of the air-saturated and degassed solutions, respectively. In order to avoid minor fluctuations, the lifetimes used in eq 1 were obtained from smoothed Arrhenius plots such as that of Figure 1. Below  $-150^\circ$  the phosphorescence lifetimes of the air-saturated and deoxygenated samples were indistinguishable for all of the complexes studied. At this temperature the solvent is rigid.

The quenching rate constants,  $k_q$ , so obtained are shown in Figure 3 as a function of temperature. Data for the two complexes  $[\text{Cr}(\text{en})_3]^{3+}$  and  $[\text{Cr}(\text{tn})_3]^{3+}$  do not appear in Figure 3. As is apparent from the observations recorded in Figure 1, the lifetimes of the air-saturated and deoxygenated solutions were identical within experimental error at all temperatures. No change in lifetime was observed even when the oxygen concentration was increased fivefold by saturation of the solution with pure oxygen at  $0^\circ$ . The values of the quenching constants for these two complexes must be at least one order of magnitude less than those for  $[\text{Cr}(\text{CN})_6]^{3-}$ .

As shown by the linearity of the  $\log k_q$  vs.  $1/T$  plots in Figure 3, the temperature dependence of the quenching rate constants fits an Arrhenius equation. Within experimental uncertainty ( $\pm 1 \text{ kcal/mol}$ ), all of the activation energies so obtained are equal and further are equal to the activation energy for solvent fluidity, 6 kcal/mol. This suggests that the temperature dependence of the quenching is governed only by the change in viscosity of the solvent with temperature and that therefore the quenching is diffusion limited.

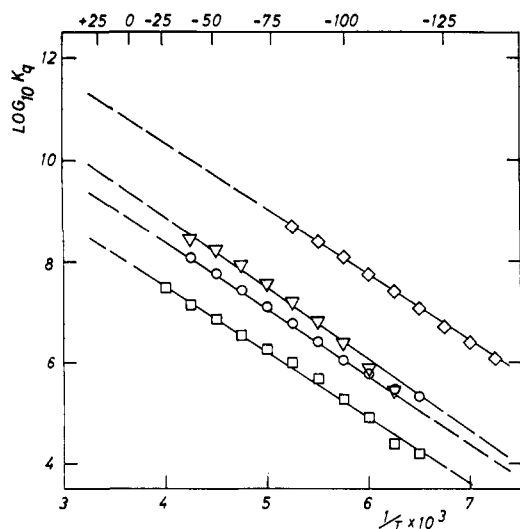


Figure 3. Temperature dependence of the quenching constants of  $[\text{Cr}(\text{acac})_3]$ ,  $\diamond$ ;  $\text{K}_3[\text{Cr}(\text{NCS})_6]$ ,  $\nabla$ ;  $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ,  $\circ$ ; and  $\text{K}_3[\text{Cr}(\text{CN})_6]$ ,  $\square$ ; in methanol, water, and ethylene glycol (2:1:1) solvent.

In one case, that of  $[\text{Cr}(\text{acac})_3]$ , the value of  $k_q$  even exceeds somewhat that found by Ware<sup>17</sup> for a comparable solvent at 25° (Table I). This discrepancy may be

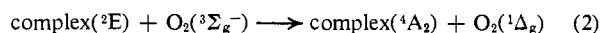
**Table I.** Energies of  $^3\text{E}$  (kcal) (1), Quenching Constants ( $M^{-1} \text{sec}^{-1}$ ) Extrapolated to 25° (2), and Observed Activation Energies (kcal mol<sup>-1</sup>)

| Compound  | Energy <sup>a</sup> of $^3\text{E}$ | Quenching constant              | Activation energy |
|---|-------------------------------------|---------------------------------|-------------------|
| $[\text{Cr}(\text{tn})_3]^{3+}$                             | 43.1                                | ( $\leq 10^7$ )                 |                   |
| $[\text{Cr}(\text{en})_3]^{3+}$                             | 4.26                                | ( $\leq 10^7$ )                 |                   |
| <i>trans</i> - $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ | 38.1                                | $2 \times 10^9$                 | 6.1               |
| $[\text{Cr}(\text{NCS})_6]^{3-}$                            | 36.7                                | $6 \times 10^9$                 | 7.1               |
| $[\text{Cr}(\text{acac})_3]$                                | 36.7                                | $10^{11}$                       | 6.1               |
| $[\text{Cr}(\text{CN})_6]^{3-}$                             | 35.5                                | $2 \times 10^8$                 | 5.7               |
| Solvent   |                                     | $2 \times 10^{10}$ <sup>b</sup> | 6                 |

<sup>a</sup> From ref 9 and H. L. Schlaefer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967). <sup>b</sup> Determined for 2-propanol, from ref 17.

the result of the long extrapolation of the  $k_q$  data for  $[\text{Cr}(\text{acac})_3]$  to room temperature. Although the activation energies are the same for the four complexes  $[\text{Cr}(\text{acac})_3]$ ,  $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ,  $[\text{Cr}(\text{NCS})_6]^{3-}$ , and  $[\text{Cr}(\text{CN})_6]^{3-}$ , the quenching efficiencies are not the same. In fact, they span three orders of magnitude. At -90°, for example, the values of  $k_q$  are  $2 \times 10^8$ ,  $2 \times 10^6$ ,  $5 \times 10^6$ , and  $3 \times 10^5 M^{-1} \text{sec}^{-1}$ , respectively.

On the basis of energetics and spin conservation (or correlation), the quenching reaction is most likely to be



The  $^1\Delta_g$  state of oxygen has an energy of 22.6 kcal<sup>18</sup> so that reaction 2 is exothermic for all chromium(III) complexes. This reaction has been verified by esr studies for the quenching of anthracene (and derivatives) triplet-state molecules by oxygen.<sup>4-6</sup> The energy transfer quenching in eq 2 will be a short-ranged interaction; therefore its efficiency will be sensitive both to

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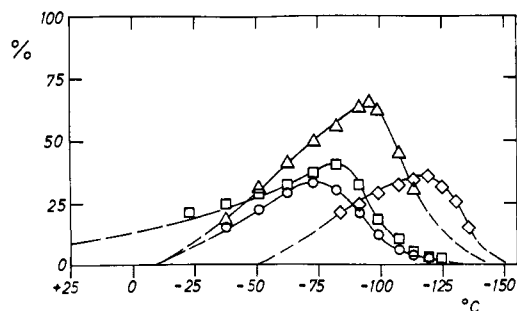


Figure 4. Temperature dependence of the amount of quenching (%) of  $[\text{Cr}(\text{acac})_3]$ ,  $\diamond$ ;  $\text{K}_3[\text{Cr}(\text{NCS})_6]$ ,  $\Delta$ ;  $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ,  $\circ$ ; and  $\text{K}_3[\text{Cr}(\text{CN})_6]$ ,  $\square$ ; in methanol, water, and ethylene glycol (2:1:1) solvent (air saturated).

the nature and size of the ligands and to the extent of solvation of the complex.

As the energy transfer does involve spin conservation, it should be hindered by the "insulating" ligands en, tn, and  $\text{NH}_3$ , and promoted by the "conducting" ligands  $\text{CN}^-$ ,  $\text{NCS}^-$ , and acac. This terminology is that used by Condrate and Forster<sup>19</sup> to describe the absence of intermolecular effects with "insulating" ligands. We have noted that while the decay of phosphorescence is strictly exponential for crystalline complexes with the ligands en, tn, and  $\text{NH}_3$ , the decays are more complex with ligands  $\text{CN}^-$  and  $\text{NCS}^-$ , except in dilute crystals.<sup>20</sup> The assumption above is in agreement with the experimental results. A similar observation was made by Ohno and Kato,<sup>21</sup> who found that aromatic ligands of  $\text{Cr}(\text{III})$  complexes enhanced the rate of energy transfer from organic triplets.

Even among the complexes with conducting ligands, the quenching rate constants are quite different.  $[\text{Cr}(\text{acac})_3]$  has a quenching constant close to the maximum calculated for a diffusion-controlled reaction. Since it is neutral, the complex is not hydrated to any appreciable extent in the polar solvent used. There is therefore little hindrance to an attack by oxygen via the  $\pi$ -electron system involving the  $t_{2g}$  orbitals. Both  $[\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{NCS})_6]^{3-}$  must be appreciably hydrated (the solvent has a mole fraction of water of about 0.3). The insulating effect of this hydration sphere is reflected in quenching efficiencies considerably lower than that for  $[\text{Cr}(\text{acac})_3]$ . The quenching constants of the three complexes  $[\text{Cr}(\text{acac})_3]$ ,  $[\text{Cr}(\text{NCS})_6]^{3-}$ , and  $[\text{Cr}(\text{CN})_6]^{3-}$  extrapolated to room temperature are compared in Table I. This situation is in marked contrast to that for organic systems, in which rate constants less than diffusion-controlled arise only when the quenching (or energy transfer) reaction is endothermic.<sup>22</sup> A similar dependence of quenching rate constant on charge of the complex was found by Wasgestian and Hammond<sup>23</sup> with various aromatic hydrocarbons in triplet states as donors and chromium(III) complexes as acceptors. They have interpreted their data in terms of a dipole-quadrupole resonance energy transfer. However, the case of the  $\text{O}_2$  quenching of the

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emission of the Reineckate ion is not so clear. The lower charge should lead to less hydration than for  $[\text{Cr}(\text{NCS})_6]^{3-}$ , but to counteract this effect is the fact that there are fewer conducting ligands. The quenching constants for these two complexes at room temperature differ by a factor of 3 (Table I).

In Figure 4 the amount of quenching in air-saturated solutions is plotted as a function of temperature and extrapolations are made to room temperature. Owing to its long lifetime, quenching is stronger for  $\text{K}_3[\text{Cr}(\text{CN})_6]$ . When the temperature is raised other modes of deactiva-

tion compete with quenching. At  $-10^\circ$  quenching is negligible for most complexes except for  $\text{K}_3[\text{Cr}(\text{CN})_6]$ , which is still sufficiently long lived to be quenched by oxygen. The amount is approximately 10–15% at room temperature and hence experiments in photochemistry dealing with this complex at room temperature should be carried out in degassed solutions.

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## $^{119}\text{Sn}$ Chemical Shifts by the Double Resonance of Organotin Compounds

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**Abstract:** Tin-119 chemical shifts in 40 organotin compounds have been obtained by  $^1\text{H}-\{^{119}\text{Sn}\}$  double-resonance experiments. The tin-119 shifts for organotin compounds where tin is bonded to hydrogen, lithium, and phosphorus atoms are reported along with those for the organotin acetylene, perfluoroalkyl, and perchlorophenyl derivatives for the first time. The most downfield tin shift thus far reported has been measured for the dimethyl-dithiolatotin(IV) heterocycle. Previously drawn correlations with electronegativity are tested with respect to the new substituents. Dispersion forces and effects due to neighboring polarizable groups are seen to be important in raising the shift as with the iodides and unsaturated systems. Higher coordination at tin produces large, upfield shifts, but the cationic organotin complexes appear less shielded than the neutral or anionic complexes.  $^{119}\text{mSn}$  Mössbauer quadrupole splitting and  $J(^{119}\text{Sn}-^{19}\text{F})$  data are used to establish *intramolecular* coordination in the perfluoroethyl derivatives which are characterized by large, upfield tin shift values.

The first tin chemical shifts were measured by direct observation on 18 compounds by Burke and Lauterbur in 1960.<sup>2</sup> Precise values were difficult to obtain because of the small natural abundance of the magnetic tin-119 isotope (8.7%) and the low sensitivity and long relaxation times with the resulting saturation problems associated with this nucleus. Hexamethylditin<sup>3</sup> and hexamethyldistannoxane<sup>4</sup> were examined by the same method. In 1968 Hunter and Reeves obtained the tin-119 shifts of 39 additional organotin compounds by direct observation, with enhancement of the signals by heteronuclear decoupling in the proton region.<sup>5</sup> In 1969 McFarlane, *et al.*, used  $^1\text{H}-^{119}\text{Sn}$  double resonance to obtain the tin shifts of 49 additional compounds.<sup>6</sup> Several advantages follow from the use of this indirect method, among which are that (a) the precision of the measurements is greatly improved, (b) saturation is no longer a problem, and (c) spin-spin coupling relationships between the proton and tin nuclei can be determined.

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We report in this paper the tin-119 shifts of 37 organotin compounds measured by heteronuclear decoupling experiments of the  $^1\text{H}-\{^{119}\text{Sn}\}$  type. From the data on the 108 compounds in the literature it is known that in general electron withdrawal tends to lower the tin shift while increasing the coordination number at tin tends to raise it. These general trends are also features of the spectra of other magnetic nuclei of the fourth group such as  $^{13}\text{C}$ ,<sup>7</sup>  $^{29}\text{Si}$ ,<sup>5,7,8</sup> and  $^{207}\text{Pb}$ .<sup>7,8</sup>

### Results

Table I lists the tin-119 chemical shift values of 40 organotin compounds, 37 reported here for the first time, in decreasing order of shift, with tetramethyltin taken as zero. The values of  $\Xi$ , defined as the resonant frequency in a polarizing magnetic field of strength such that  $(\text{CH}_3)_4\text{Si}$  gives a proton resonance of exactly 100 MHz,<sup>9</sup> are also listed. Most of the compounds could be recorded as solutions in the noninteracting solvents benzene and methylene dichloride because of the high sensitivity of the double-resonance method. The diamagnetic anisotropy of benzene which can give rise to shifts of up to 1 ppm in proton spectra can be

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