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KINETICS OF OXIDATIVE ADDITION OF ZEROVALENT PALLADIUM TO AROMATIC IODIDES

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Summary

The kinetics of oxidative addition of zerovalent palladium to aromatic iodides in tetrahydrofuran in the presence of the ligand triphenylphosphine have been studied by amperometry on the oxidation wave of palladium. The reaction is first order in aromatic iodide and first order in palladium and the rate constant is inversely proportional to the free ligand concentration. The reactive palladium intermediate is assumed to be $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$. This assumption is compatible with the observed activation parameters $\Delta H^\ddagger = +77 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = 13 \text{ J mol}^{-1} \text{ K}^{-1}$. With substituted aromatic iodides, the rate constants give a linear Hammett relationship with $\rho = +2$. The suggested mechanism can be regarded as related to an aromatic nucleophilic substitution with some assistance from halogen–palladium interaction.

1) Introduction

Oxidative addition of low-valent transition metal complexes to aromatic halides is a key step in many synthetic applications [1], but experimental difficulties have allowed only a few kinetic studies.

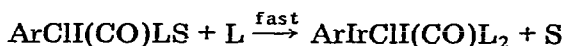
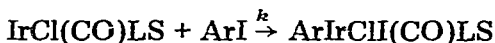
R.J. Mureinik et al. studied the kinetics of the oxidative addition of Vaska's complex, *trans*- $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$, to six aryl iodides [2]. The reaction was followed by UV spectrometry of Ir^{I} at 387 nm and was conducted in a sealed cell at 140–150°C. In presence of excess aryl iodide and variable amounts of $\text{P}(\text{C}_6\text{H}_5)_3$, the reaction was pseudo-first order in Vaska's complex and the observed rate constant k_{obs} was expressed by

$$k_{\text{obs}} = k_1 + k_2(\text{ArI}) \quad \text{with } k_2 = \frac{kK}{K + [\text{P}(\text{C}_6\text{H}_5)_3]}$$

This rate law was interpreted in terms of two parallel reaction schemes as follows. The first scheme does not involve ligand dissociation:

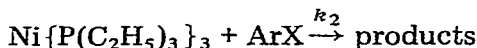
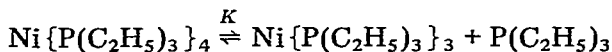


The second scheme involves ligand dissociation:



A plot of $\log k_2$ versus Hammett σ gives $\rho = +0.4$.

J.K. Kochi studied the kinetics of the reaction of $\text{Ni}\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$ with aromatic halides, ArX , following the disappearance of the UV absorption of this Ni^0 complex which strongly absorbs at 500 nm [3]; he interpreted the rate law in terms of the following scheme:



Hammett plots gave ρ values rising in the order $\text{ArI} < \text{ArBr} < \text{ArCl}$, i.e. $\rho = +2.0; +4.4; +5.4$, respectively. A ρ value as high as +5.4 was interpreted as an indication of a highly negatively charged transition state, very close to a radical anion, resulting from an outer-sphere electron transfer process. The Hammett correlations were not very good, however, and were based on only a small range of σ values: for iodobenzenes in THF from $\sigma \simeq +0.18$, $\log k \simeq 1.6$ at one extreme, to $\sigma \simeq +0.36$, $\log k \simeq 2.8$ at the other (from ref. 3, Fig. 5). Kochi reported the electrochemical oxidation wave of zerovalent nickel but did not use it for monitoring the reaction [3].

We reported the electrochemical oxidation characteristics of $\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ in tetrahydrofuran (THF) or ethanol [4] and used them for studying the kinetics of oxidative addition of zerovalent nickel with aromatic halides. The reaction was found to be first order in $\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ and in ArX . Since $\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ neither associates with $\text{P}(\text{C}_6\text{H}_5)_3$ nor dissociates into $\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ in THF in the range of concentrations we studied, the rate was independent of the $\text{P}(\text{C}_6\text{H}_5)_3$ concentration. Hammett plots were not assessed quantitatively. Activation energies were in the range of 40 to 70 kJ mol^{-1} .

Wishing to compare the behaviour of nickel and palladium complexes, we undertook a similar study with zerovalent palladium-triphenylphosphine complexes and we now report our results on the kinetics of oxidative addition of aromatic iodides.

2) Results

2.1.) Electrochemical oxidation of zerovalent triphenylphosphine palladium complexes

Although they have a slight yellow colour, triphenylphosphine-palladium complexes do not show strong characteristic UV-visible absorption at wavelengths longer than those corresponding that of triphenylphosphine. This prevents easy UV assay of palladium complexes, either of the $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_n$ or the $\text{ArPdX}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ type.

In THF, the complexes $\text{ArPdX}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ do not show characteristic oxidation or reduction electrochemical properties, but zerovalent $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ does. To our knowledge, its electrochemical properties have not previously been reported, presumably because of experimental difficulties.

In the presence of excess triphenylphosphine (10^{-2} to 1 molar) under argon at room temperature or above (20 to 50°C), in THF containing $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ as a supporting electrolyte, zerovalent palladium $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4$ (dissociated to $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ and $\text{P}(\text{C}_6\text{H}_5)_3$ in solution [5]) shows at a rotating or static platinum microelectrode an irreversible, bielectronic, diffusion controlled, oxidation wave at -0.47 V versus an AgClO_4/Ag electrode (Fig. 1) whose height is stable with time and reproducibly proportional to the palladium concentration (10^{-4} to 10^{-2} molar) to better than $\pm 2\%$. More detailed electrochemical properties of palladium complexes will be published elsewhere, but we should mention presently some experimental pitfalls which can be easily avoided.

Without added triphenylphosphine, solutions of $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4$ in THF are not indefinitely stable and results are irreproducible. Oxygen, pure or from the

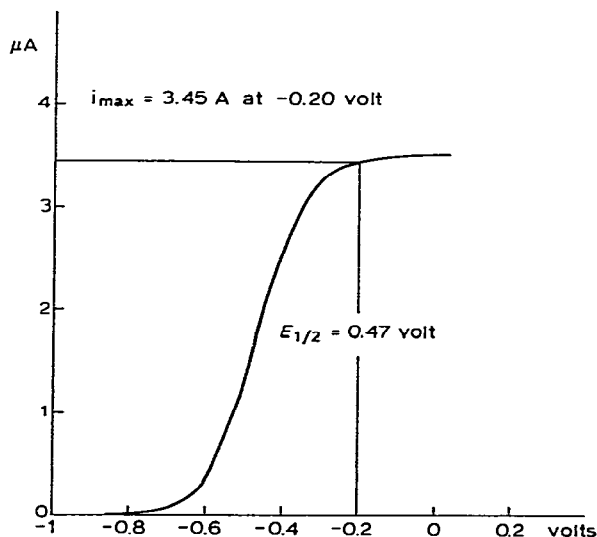


Fig. 1. Voltamperogram of $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ in THF against a AgClO_4/Ag electrode with $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ as supporting electrolyte.

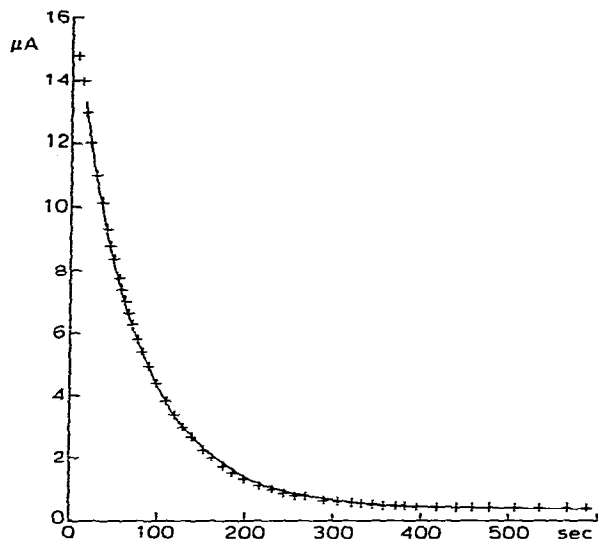


Fig. 2. Typical kinetic curve for the reaction of Pd^0 with ArI . $[\text{Pd}^0]_0 = 2.10^{-3} M$; $[\text{C}_6\text{H}_5\text{I}]_0 = 10^{-2} M$; $[\text{P}(\text{C}_6\text{H}_5)_3] = 0.1 M$. Temperature 25°C + experimental; — calculated.

air, bubbled into the solution forms a complex, reportedly $\text{PdO}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ [6], oxidable at -0.25 V versus AgClO_4/Ag . This complex is not very stable in solution, especially in absence of excess phosphine; bubbling argon into the solution regenerates the original complex, characterized by its oxidation wave at -0.47 V. Contact with oxygen must thus be avoided. We observed no modification of the electrochemical properties of palladium when changing from argon to nitrogen.

At low temperature, the possible passivation of the electrode must be kept in mind.

2.2.) Kinetic results

The oxidative addition of $\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ with aromatic iodides, ArI , was a

TABLE I
RATE CONSTANTS FOR DIFFERENT INITIAL CONCENTRATIONS OF IODOBENZENE ^a

Initial concentration of iodobenzene (mole/l)	Rate constant (l/mole/sec)
1.89×10^{-3}	0.87
3.15×10^{-3}	0.79
6.30×10^{-3}	1.01
1.26×10^{-2}	0.93
2.52×10^{-2}	0.85
4.72×10^{-2}	0.96
9.45×10^{-2}	0.89
1.89×10^{-1}	0.78

^a Initial concentration of zerovalent Palladium = 1.06×10^{-3} mole/l. Concentration of added triphenylphosphine = 0.1 mole/l. Temperature = 25.0°C .

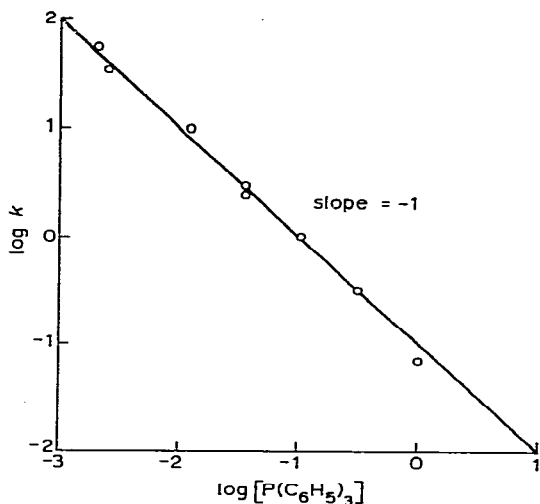


Fig. 3. Relationship between $\log k$ and $\log [P(C_6H_5)_3]$. $[Pd^0]_0$: 1 to $2.10^{-3}M$; $[C_6H_5I]$: $10^{-2} M$; temperature $25^\circ C$.

second order process, first order in zerovalent palladium and first order in aromatic iodide. The rate constant was computed by a least-squares method. The concentration of zerovalent palladium, Pd^0 measured by amperometry against time shows excellent agreement with the calculated best-fitting curve (Fig. 2).

Rate constants were determined for various ratios of initial concentrations $[ArI]_0/[Pd^0]_0$ from 2 to 200 approximately, with a constant $P(C_6H_5)_3$ concentration of $0.1 M$. Only random deviations were observed from the mean value $k = 0.9 \text{ mol}^{-1} \text{ l sec}^{-1}$ (Table 1).

For $P(C_6H_5)_3 < 1 M$, the rate constant is inversely proportional to the tri-

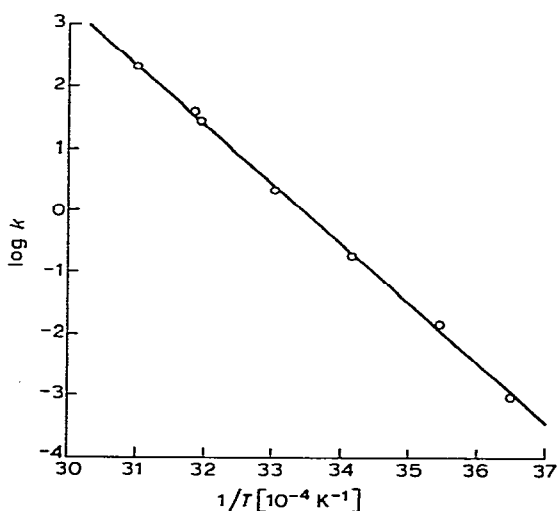


Fig. 4. Arrhenius Plot. $[P(C_6H_5)_3]$: $0.1 M$; $[C_6H_5I]_0$: $10^{-2} M$; $[Pd^0]_0$: 1 to $2 \times 10^{-3} M$.

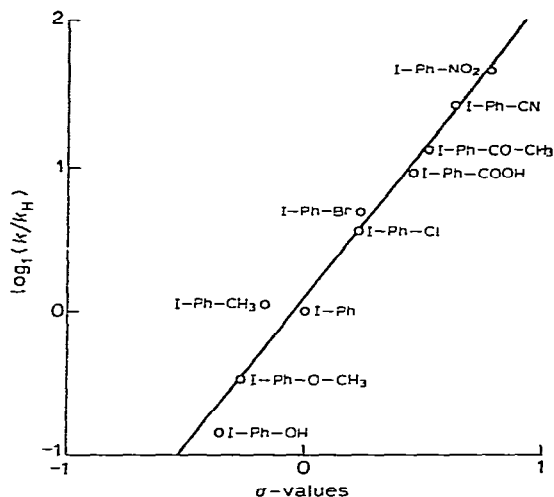


Fig. 5. Hammett plot. $[P(C_6H_5)_3]$: 0.1 M; $[ArI]$: 10^{-2} M; $[Pd^0]_0$: 2.10^{-3} M, temperature 25° C. All the iodo arenes are *para*-substituted.

phenylphosphine concentration (Fig. 3). For small values of $[P(C_6H_5)_3]$ this value was taken to be $[P(C_6H_5)_3]_{added} + [Pd^0]_0$ since zerovalent palladium was added as $Pd\{P(C_6H_5)_3\}_4$ which dissociates into $Pd\{P(C_6H_5)_3\}_3 + P(C_6H_5)_3$.

For the reaction of Pd^0 and C_6H_5I , with $[P(C_6H_5)_3] = 0.1$ M, k was measured for temperatures in the range $0-50^\circ$ C. Fig. 4 shows the relationship obtained when $\ln k$ is plotted against $1/T$. The Arrhenius equation $\ln k = \ln A - E/RT$ gives $\ln A = 32.13$ and $E = 79.5$ kJ mol $^{-1}$.

Classical equations for the enthalpy and entropy of activation yield for an average temperature of 300 K give $\Delta H = 77$ kJ mol $^{-1}$ and $\Delta S = 13$ J mol $^{-1}$ K $^{-1}$.

The rate constants for the oxidative addition of a series of *para*-substituted iodobenzenes were measured at 25° C, with $[P(C_6H_5)_3] = 0.1$ M. Figure 5 shows the values of $\log k$ plotted against the Hammett σ constant [7]. The correlation is good (0.986), and gives a ρ value of +2.0.

As aromatic bromides are less reactive than iodides, rate constants were measured only for the oxidative addition with *para*-bromocyanobenzene. Under the same conditions, the rate constant ratio for *para*-bromocyanobenzene/*para*-iodocyanobenzene is ca. 2×10^{-4} at 25° C. No attempt was made to obtain data for aromatic chlorides, which are even less reactive.

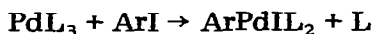
3) Discussion

First we would emphasize the value of the electrochemical method for following the zerovalent palladium concentration. The method is specially valuable in the presence of other substrates absorbing in the UV range such as triphenylphosphine $P(C_6H_5)_3$ (designated by L below). The method is sufficiently sensitive and reproducible, and there is no interference from the reaction products.

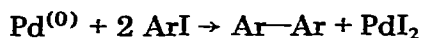
Use of a computer allows easy treatment of second-order kinetics under far from pseudo first-order conditions. Comparison of calculated and experimental

points is excellent, even well beyond 50% of reaction with initial concentrations of Pd⁰ and ArI in the same range. There is no kinetic evidence for any stoichiometry other than one palladium atom for one aromatic iodide molecule, at least when an excess of aryl iodide is used.

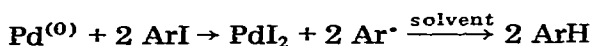
Under our experimental conditions, we were unable to detect by GLC any aromatic hydrocarbon, Ar-H or Ar-Ar, formed during the reaction, although such products have been detected in the reaction of zerovalent nickel complexes with aromatic halides [3]. Thus we assume the reaction to be solely as follows:



without side reactions such as

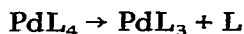


or

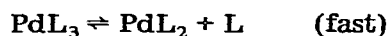


Thus, if any radical Ar[•] or anion Ar⁻ is formed during the reaction, it must be scavenged by the palladium before reacting with the solvent or another radical. This suggests that under our conditions the reaction does not proceed via "free" radicals. This point will be discussed later.

The observed kinetic constant *k* is strictly inversely proportional to the free phosphine concentration calculated by assuming complete dissociation.



We do not observe significant deviation from linearity in Fig. 3, even for low phosphine concentrations ($2 \times 10^{-3} M$, i.e. no added free phosphine). This observation is compatible with the following scheme:



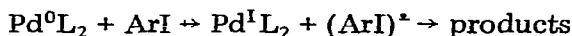
The pre-equilibrium is necessary to explain the rate dependence on phosphine concentration. Since the rate is first order in ArI at the available experimental precision, the pre-equilibrium must be fast, with PdL₃ unreactive and only slightly dissociated into reactive PdL₂. The equilibrium constant cannot be obtained by our techniques, but evidence for such reactive 14 electron complexes have been obtained by Mann and Musco [5] for similar complexes of palladium.

According to this scheme, the observed activation parameters ΔH^\ddagger and ΔS^\ddagger represent the sum of ΔH^0 (or ΔS^0) for the pre-equilibrium and of ΔH_1^\ddagger (or ΔS_1^\ddagger) for the reaction of PdL₂ + ArI. The experimental values are in the expected range, since both reactions should have large positive enthalpies but ΔS^0 and ΔS_1^\ddagger should be of the same absolute magnitude and of opposite sign. Scheme 1 is thus supported by the experimental values of the activation parameters, since ΔH^\ddagger would be too high and ΔS^\ddagger too low for a one step mechanism, such as $\text{PdL}_3 + \text{ArI} \rightarrow \text{ArPdIL}_2 + \text{L}$.

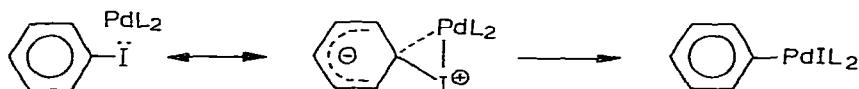
The Hammett plot, with $\rho = 2$, sheds light on the second step only. A positive value indicates some electron density transfer to the aromatic ring in the transition state. In the case of zerovalent nickel complexed with tributylphosphine and aromatic iodides ($\rho = 2$), Kochi suggests that this transfer corresponds to one electron. Effectively monovalent nickel complexes and ArH could be detected in this reaction [3].

Zerovalent nickel is a strong reducing agent. In ethanol $\text{Ni}^{\text{I}}\text{L}_2\text{Br}$ is reversibly reduced into zerovalent nickel at -0.8 V versus SCE via a monoelectronic process (4c). Even so, we never observed products from a radical pathway in the reaction of Ni^0L_3 with ArX in THF [4], although we confirmed the possibility of a radical pathway in the reaction between $\text{Ni}^0\{\text{P}(\text{n-C}_4\text{C}_9)_3\}_3$ and ArX [8].

Zerovalent palladium appears not to be as effective a reducing agent as zerovalent nickel, but we lack electrochemical reversible data for comparison. With triphenylphosphine we did not detect any monovalent palladium, either chemically or electrochemically. Neither did we observe in our reaction products which could be ascribed to the formation of Ar^\cdot . So we suggest that the reaction of zerovalent palladium with aromatic iodides does not proceed via a rate controlling monoelectronic transfer:



In our opinion, PdL_2 is a 14 electron complex able to accept an electron pair from the iodine moiety (Ar_3P , Ar_2S , ArX are isoelectronic on the heteroatom and their coordinating power is $\text{Ar}_3\text{P} > \text{Ar}_2\text{S} > \text{ArX}$). The palladium atom could then share an electron pair with a π -antibonding molecular orbital, transiently affecting the sp^2 character of the aromatic C—X bond and transferring negative charge from iodine to the ring without much affecting the charge in palladium.



This mechanism bears strong similarities to nucleophilic aromatic substitution, except that it proceeds more easily with iodine than with bromine or chlorine, perhaps because the iodine moiety is more electropositive, is a better ligand for the soft zerovalent palladium moiety, or because it is more polarisable and the C—I bond more easily broken.

4) Experimental

4.1. Chemicals

$\text{Pd}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4$ was prepared following the method of Malatesta [9] by reducing Na_2PdCl_4 in ethanol with NaBH_4 in presence of an excess of triphenylphosphine. Iodobenzene was distilled in vacuo; other aromatic halides, commercially available (K&K, Pfalz and Bauer), were generally used without further purification. Tetrahydrofuran (Merck) was distilled over sodium naphthalide in a nitrogen atmosphere immediately before use. Tetrabutylammonium perchlorate (TBAP) (Fluka) was used without further purification.

4.2.) Electrochemistry

Since zerovalent palladium is air-sensitive, all measurements were performed under argon. The supporting electrolyte was TBAP. The three electrode method was used: the monitoring electrode was a rotating platinum disc 1 mm diameter; the counter electrode was a platinum wire; the reference electrode was a silver wire in a solution of AgClO_4 (0.1 M) + TBAP (0.1 M) in THF, separated from the bulk solution by a sintered disk. Conventional electrochemical equipment (Tacussel) were used.

4.3.) Check for presence of Ar-H

For convenience, the check was made for the reaction involving *para*-iodocyanobenzene. In 28.5 ml of THF solution at 25°C containing 1 g TBAP (0.1 M), 0.75 g $\text{P}(\text{C}_6\text{H}_5)_3$ (0.1 M), 330 mg $\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_4$ (10^{-2} M, 0.285 mmol) is added 130 mg *para*-iodocyanobenzene ($2 \cdot 10^{-2}$ M, 0.565 mmol). Amperometry shows that the reaction is complete in a few seconds. Biphenyl (65 mg) is added as internal standard, 50 ml water is added and the mixture extracted with diethyl ether (2×20 ml). After drying over sodium sulfate and concentration of the solution, neither $\text{C}_6\text{H}_5\text{CN}$ nor $\text{NCC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CN}$ could be detected by gas chromatography.

4.4.) Kinetics

The temperature was maintained within $\pm 0.1^\circ\text{C}$. The kinetic data are imprecise at the reaction beginning (mixing of the reactants) and at the end (residual current). A computer program was written with three unknowns: rate constant, residual current at infinite time, and origin of time, calculated by a least square deviation method. A Tektronix 4051 calculator was used for calculations, the best-fitting plots were drawn on a Tektronix 4662 plotter.

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