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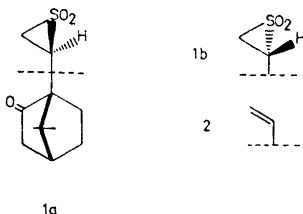
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Epimeric 2-[(1S)-7,7-Dimethyl-2-oxo-1-norbornanyl]-thiirane-1,1-dioxides

TOMAS KEMPE and TORBJÖRN NORIN

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

The reaction between diazomethane and the intermediate sulphene produced by treatment of (1S)-camphor-10-sulphonyl chloride with triethylamine has been reported to give a thiiranedioxide (m.p. 83–85°).^{1,2} We have repeated this experiment. The two epimeric thiiranedioxides (*1a* and *1b*) thus formed have now been separated by thin layer and column chromatography on silica gel. The mixture of epimers as well as each of the two pure isomers decomposed when heated above their melting points yielding the known (1S)-7,7-dimethyl-1-vinyl-2-norbornanone (*2*).^{1,2}



Experimental. 2-[(1S)-7,7-dimethyl-2-oxo-1-norbornanyl]-thiirane-1,1-dioxides (*1a* and *1b*). The mixture of the epimeric thiiranedioxides (*1a* and *1b*) was prepared from (1S)-camphor-10-sulphonyl chloride (m.p. 67–68°; $[\alpha]_D^{21} + 30^\circ$, *c* 2.0 in CHCl₃) according to the procedure of Opitz and Fischer.^{1,2} The two compounds could be separated by TLC (Merck Silica gel HF₂₅₄), e.g. when eluted with ethyl ether, *R_F* values were 0.55 and 0.77. The epimers were separated on preparative scale by column chromatography (silica gel/ethyl ether) to yield a low-melting isomer (*R_F* 0.77; m.p. 81–86° dec.; approximate yield 70%; $[\alpha]_D^{21} - 5.6^\circ$, *c* 3.1 in CHCl₃) and a high-melting isomer (*R_F* 0.55; m.p. 100–106° dec.; approximate yield 15%; $[\alpha]_D^{21} - 58.6^\circ$, *c* 0.8 in CHCl₃). The two isomers exhibited similar IR spectra: ν (CHCl₃) 1735 (C=O), 1320 and 1160 (SO₂) cm⁻¹.² The compounds were insufficiently stable at room temperature for meaningful elemental analysis. However, they could readily be characterized by heating to yield (1S)-7,7-dimethyl-1-vinyl-2-norbornanone (*2*) (m.p. 65–66°; $[\alpha]_D^{21} + 16^\circ$, *c* 3.3 in CHCl₃).^{1,2}

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On the Electrical Properties of Pd₁₇Se₁₅, Pt₅Se₄, and PtTe

ARNE KJEKSHUS

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

Only sparse information is available on the low temperature electrical behaviours of transition metal pnictides and chalcogenides. Moreover, the few investigations hitherto have been concerned with phases having relatively simple compositions and crystal structures. Therefore, it was considered worthwhile to study a few phases which do not satisfy the above

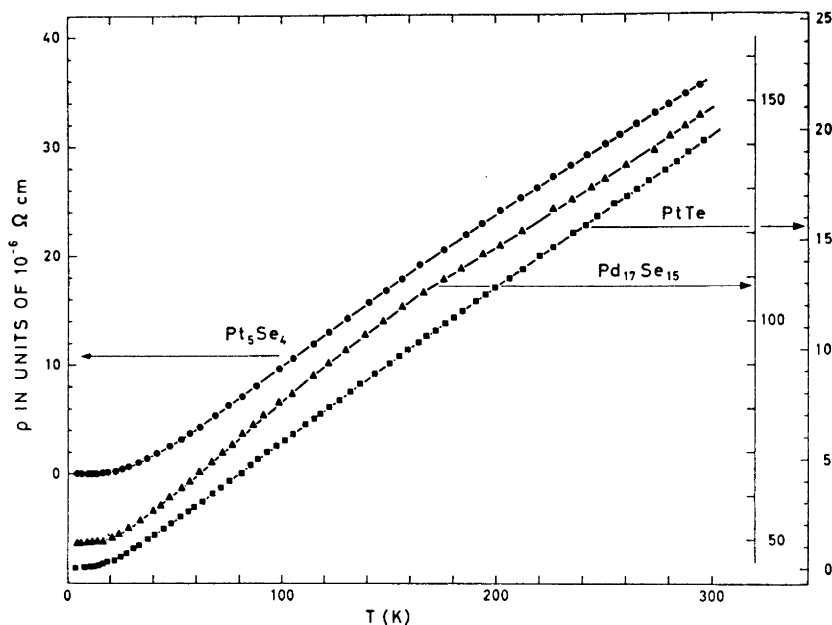


Fig. 1. Electrical resistivity of $\text{Pd}_{17}\text{Se}_{15}$, Pt_5Se_4 , and PtTe as a function of temperature.

criteria. $\text{Pd}_{17}\text{Se}_{15}$, Pt_5Se_4 , and PtTe were chosen as suitable candidates for examination, since as opposed to the structural¹⁻⁵ and magnetic^{1,3} studies no electrical measurements have been published.

Experimental. Polycrystalline samples were made by heating weighed quantities of the elements (99.999 % Pd and Pt (Koch-Light Laboratories), 99.998 % Se (Bolidens Gruvaktiebolag), and 99.999 % Te (American Smelting and Refining Co.)) in evacuated, sealed quartz tubes. During the syntheses, the temperature was slowly increased to 600°C in the case of $\text{Pd}_{17}\text{Se}_{15}$ and 850°C for Pt_5Se_4 and PtTe , the samples were kept at these temperatures for 10 days, and then quenched in ice water.

The experimental details concerning the zone melting and crystal cutting procedures and the measurements of electrical resistance and temperature were performed as described in Ref. 6 and references therein.

Results. X-Ray and microscopical examination showed that the $\text{Pd}_{17}\text{Se}_{15}$ and Pt_5Se_4 samples consisted of a single phase,

whereas globular inclusions of a second phase occurred in the PtTe sample. After some difficulties it proved possible to cut essentially single crystal specimens of the three compounds.

The temperature dependence of the electrical resistivity of $\text{Pd}_{17}\text{Se}_{15}$, Pt_5Se_4 , and PtTe is shown in Fig. 1. The curves were reproducible for conditions of both decreasing and increasing temperature whenever repeated measurements were performed on the *same* sample. The results obtained for different specimens vary somewhat, the effect being most marked for PtTe , least for Pt_5Se_4 . This is provisionally attributed to anisotropy in ρ , but can equally well be due to variation in specimen homogeneity and/or crystalline perfection. Further investigations are required to clarify this point.

The residual resistance ratios ($R_{4,2}/(R_{293} - R_{4,2})$) of the various $\text{Pd}_{17}\text{Se}_{15}$ specimens were never better than about $\frac{1}{2}$, as opposed to the ratios of approximately 6.1×10^{-3} and 2.2×10^{-3} for the measured samples of Pt_5Se_4 and PtTe , respectively. The temperature coefficients, $\alpha = (1/\rho_{273})(d\rho/dT)$, calculated from the linear por-

tions of the $\rho(T)$ -curves are $2.8_1 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ (30–150 K) and $2.2_3 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ (180–300 K) for $\text{Pd}_{17}\text{Se}_{15}$, $4.3_2 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ (50–160 K) and $3.9_3 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ (180–300 K) for Pt_5Se_4 , and $3.9_5 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ (40–300 K) for PtTe . Hence, the temperature dependences of ρ for $\text{Pd}_{17}\text{Se}_{15}$ and Pt_5Se_4 differ from that of PtTe in that the former curves are slightly concave towards the temperature axis. In line with earlier suggestions^{6–10} this behaviour (which is commonly found for phases comprising palladium) is tentatively attributed to *s-d* interband scattering.

Using the procedure of Kelly and MacDonald,¹⁰ the characteristic temperatures θ_R derived from the $\rho(T)$ -curves of Pt_5Se_4 and PtTe are approximately 190 and 230 K, respectively. The θ_R -value for PtTe is in close agreement with $\theta_D = 245$ K estimated from the heat capacity data¹¹ and θ_R for Pt_5Se_4 probably differ by no more than a few per cent at most from the Debye temperature (θ_D) in the region of θ itself. The $\rho(T)$ -curve for $\text{Pd}_{17}\text{Se}_{15}$ is inconsistent with a finite value of θ_R .

Although the crystal structure of Pt_5Se_4 is hitherto unknown, the atomic arrangement of $\text{Pd}_{17}\text{Se}_{15}$ ⁴ will almost certainly prove to be the most heterogeneous (as evident from the entirely different coordinations of its three non-equivalent Pd atoms) of these compounds. Thus, the diversity in structure is paralleled by the distinctly different electrical properties of $\text{Pd}_{17}\text{Se}_{15}$ (Fig. 1 and *vide supra*).

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Homogeneous Chemical Kinetics at the Rotating Disk Electrode. Application to the Pyridination of Diphenylanthracene Cation Radical

ULLA SVANHOLM and
VERNON D. PARKER

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

The rotating disk electrode (rde) has been shown to be a versatile tool for the study of the kinetics of chemical reactions coupled to electron transfer. Pseudo first order rate constants as high as 10^9 sec^{-1} may be estimated. The rde method as well as other electrochemical methods are limited by the need to compare data to working curves obtained by calculations based on an assumed mechanism and ideal behaviour. Adams¹ has reviewed the use of the rde in studying ECE processes and cautions the practice of assigning mechanisms to reactions occurring at solid electrodes on the basis of a single electroanalytical technique. Here we report the use of the rde as an analytical device to follow the progress of a homogeneous chemical reaction.* The reaction chosen to illustrate the method is the pyridination of the 9,10-diphenylanthracene (DPA) cation radical, previously studied as a coupled chemical reaction at the rde.² This reaction is of particular interest in that studies using two different electroanalytical techniques, rde voltammetry² and chronoamperometry,³ led to conflicting results and the assignment of different mechanisms.

Rate data for seven experiments involving the reaction of $\text{DPA}^{+\cdot}$ (initial concentration 1.3 to $6.25 \times 10^{-5} \text{ M}$) with pyridine (1.0 to $5.0 \times 10^{-5} \text{ M}$) are summarized in Table 1. Pseudo first order rate constants ranging from 0.38 to 2.1 sec^{-1} were observed. The second order rate constant at $11.7 \pm 0.2^\circ$ for reaction (1) was found to be equal to $(4.5 \pm 0.9) \times 10^4 \text{ M}^{-1}$

* Polarographic methods have been used extensively to follow the kinetics of homogeneous reactions; however this appears to be the first application to the study of very fast reactions.