tions of the $\varrho(T)$-curves are $2.8_1 \times 10^{-3}$ °C^{-1} (30 – 150 K) and $2.2_3 \times 10^{-3}$ °C^{-1} (180 – 300 K) for $Pd_{17}Se_{15}$, $4.3_2 \times 10^{-3}$ °C^{-1} (50 – 160 K) and $3.9_3 \times 10^{-3}$ °C^{-1} (180 – 300 K) for Pt_5Se_4, and $3.9_5 \times 10^{-3}$ °C^{-1} (40 – 300 K) for PtTe. Hence, the temperature dependences of ϱ for $Pd_{17}Se_{15}$ 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 $\varrho(T)$-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 data [11] 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 $\varrho(T)$-curve for $Pd_{17}Se_{15}$ is inconsistent with a finite value of θ_R.

Although the crystal structure of Pt_5Se_4 is hitherto unknown, the atomic arrangement of $Pd_{17}Se_{15}$ [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 $Pd_{17}Se_{15}$ (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

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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 10^3 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. Adams [1] 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 voltammetry [2] and chronoamperometry,[3] led to conflicting results and the assignment of different mechanisms.

Rate data for seven experiments involving the reaction of $DPA^{+\cdot}$ (initial concentration 1.3 to 6.25×10^{-6} M) with pyridine (1.0 to 5.0×10^{-5} 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 $11.7 \pm 0.2°$ for reaction (1) was found to be equal to $(4.5 \pm 0.9) \times 10^4$ M^{-1}

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* 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.

Table 1. Rate data for the pyridination of DPA cation radical in acetonitrile at 11.7 ± 0.2°.

Run	10^6 (DPA$^{+\cdot}$)$_0$[a]	10^6 (DPA$^{+\cdot}$)[b]	10^6 (pyr)	k_1 (sec^{-1})	10^{-4} k_2 M^{-1} sec^{-1}.
1	6.25	3.3	50.0	2.1	4.2
2	3.5	2.5	50.0	1.8	3.6
3	5.0	4.1	20.0	1.1	5.5
4	5.0	4.1	20.0	1.0	5.1
5	4.25	3.5	20.0	0.92	4.6
6	3.25	2.9	10.0	0.46	4.6
7	1.3	1.2	10.0	0.38	3.8
					ave. 4.5

[a] Concentration at time of addition of pyridine.
[b] Concentration at time that measurements were started.

sec^{-1}. Under ECE conditions at a pyridine concentration

$$\mathrm{DPA}^{+\cdot} + \mathrm{Pyr} \xrightarrow{k} \mathrm{DPA}^{\cdot} - \mathrm{Pyr}^{+} \quad (1)$$

of 0.025 M, the pseudo first order rate constant was estimated to be about 300 sec^{-1} at 25° which translates to a second order rate constant of about 10^4 M^{-1} sec^{-1}. Thus, considering the temperature difference, it appears that the ECE estimate is about an order of magnitude lower than that found in this work.

The cation radical concentrations employed in this study by no means define the limitation of the method. We are readily able to accurately monitor cation radical concentrations lower than 10^{-8} M. Thus the limitation to the method is the rate of mixing the reactants. Since it required from 0.1 to 0.2 sec for mixing, we arbitrarily set the minimum half life to be used at about 0.3 sec (this is readily adjusted by changes in concentration of the pyridine in the present case). The latter was also about the limitation imposed by the use of pen and ink recording, it would be necessary to go to oscilloscopic recording for faster reactions. Despite the limitations described above, it is readily shown that a half life of 0.3 sec at a concentration of 10^{-8} M gives a second order rate constant of about 3×10^8 M^{-1} sec^{-1} for a reaction of the type shown in eqn. 2. Thus, the method as it was used here is capable of giving second

$$2\,\mathrm{A} \longrightarrow \mathrm{B} \quad (2)$$

order rate constants close to the diffusion controlled limit. In a flow system, it is possible to achieve mixing in about one millisecond. It is conceivable that the method can be adapted in a flow system and thus make it possible to measure second order rate constants of the order of 10^{10} M^{-1} sec^{-1}.

Needless to say, determining the kinetics of a reaction by following the decrease in concentration of a reactant in homogeneous solution has the distinct advantage over ECE methods in that the order of the reaction in reactants is readily determined. It has been pointed out that rde and chronoamperometric working curves for the ECE mechanism very closely resemble that for a disproportionation mechanism which gives a different kinetic order.[3] Thus, we are able to say definitively from our results that the reaction of the DPA cation radical with pyridine is first order in both the cation radical and pyridine, facts which neither of the previous studies [2,3] were able to demonstrate.

Experimental. DPA was reagent grade and used without further purification. Acetonitrile was purified by the method of Moe [4] and passed through a column of neutral alumina (Woelm V 200) directly into the reaction cell under an atmosphere of dry argon. Sodium perchlorate was reagent grade, dried and stored at 150°. Pyridine was reagent grade and used without further purification.

The apparatus and general procedure followed for electrolyses have been described.[5,6] The cell used both for the kinetic study and for the preparation of the acetonitrile solution of the DPA cation radical was a cylindrical, round bottom, water jacketed container with openings for the auxiliary electrode compartment, reference electrode, inert gas supply and thermometer. The auxiliary electrode compartment was removed after preparation of the cation radical and replaced by the rde. The recording device was a Watanabe XY recorder with time base.

Preparation of DPA cation radical in acetonitrile. DPA (5.0×10^{-4} M) in acetonitrile (100 ml) containing sodium perchlorate (0.1 M) was subjected to constant current electrolysis at 12.5 mA at a platinum gauze electrode for 20 sec (theoretical cation radical concentration, 2.6×10^{-5} M). The blue cation radical color did not begin to develop until after about 5 sec. The temperature was controlled by tap water at 11.7 ± 2°. After removing the auxiliary electrode compartment and placing the Beckman rde in the solution, the limiting current at the rde indicated that the $DPA^{+\cdot}$ concentration was close to 10^{-5} M.

Typical kinetic experiment (Run 3). The slow decay of the limiting current for reduction of $DPA^{+\cdot}$ was followed (rde rotation rate 100 rps) until the $DPA^{+\cdot}$ concentration fell to 5.0×10^{-6} M. Pyridine (200 μl of a 10^{-2} M solution in acetonitrile) was injected into the solution with a Hamilton spring driven syringe and simultaneously the recorder was started at a chart speed of 5 cm/sec. Mixing was complete in 0.2 sec. and the smooth current time curve which quickly approached zero current was used to determine the rate constant. A plot of log limiting current *vs.* time was linear for more than one half life.

Alternatively, a stationary Beckman Platinum Button Electrode was used as the indicator electrode. In this case the electrode was carefully situated above a rapidly rotating magnetic stirrer. The current time curve in this case was not as smooth as with the rde; however the data still fit first order plots for greater than one half life.

Time of mixing. The time of mixing the pyridine solution with the cation radical solution was determined by the time required for the limiting current for the cation radical to fall to zero when 100 μl of pyridine was injected into the solution in the same manner as described above. The time to fall to zero current was variable depending upon where and how the pyridine entered the bulk solution but generally was in the range 0.1 to 0.2 sec.

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Versuche zur Darstellung von 6-Thioacylaminopenicillansäuren

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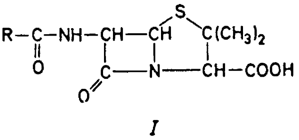
Obwohl bereits viele tausend halbsynthetische Penicilline [1] dargestellt und auf ihre antibiotische Wirksamkeit untersucht worden sind, handelt es sich ganz überwiegend um 6-Acylaminopenicillansäuren *I*. Andere Verknüpfungsarten der Aminogruppe der 6-Aminopenicillansäure sind nur vereinzelt bearbeitet worden.

Uns interessierte in diesem Zusammenhang, wieweit 6-Thioacylaminopenicillansäuren *II* und zwar insbesondere Thioanaloge biologisch aktiver *I* antibiotische Eigenschaften besitzen. Unseres Wissens liegt als einziges Material zu dieser Frage ein britisches Patent aus dem Jahre 1964 [2] vor.



I

Von den insgesamt vier in diesem Patent beschriebenen *II* ist nur eine Verbindung ein Thioanaloges einer antibiotisch wirksamen *I*, nämlich die 6-(Phenyl-thioacetyl-