placed in a separatory funnel, and the ether layer was separated and dried over sodium sulfate. After removing the ether a dark yellow oil remained. Recrystallization from alcohol of both the residue from the ether layer and the original precipitate yielded 4.1 g. (43.6%) of triphenylvinyl benzoate, melting at 151°, undepressed on mixture with triphenylvinyl benzoate synthesized by the method of Biltz.[7] The recrystallization liquors from the ester were concentrated to yield 0.4 g. (5.9%) of triphenylvinyl alcohol, identified by mixed melting point with an authentic specimen.[7]

Addition of Phenyllithium to Diphenylketene at 0°.—The same technique was followed as in the −80° addition using 0.034 mole of phenyllithium and 6.2 g. (0.032 mole) of diphenylketene[10] followed by the addition of 5.3 g. (0.038 mole) of benzoyl chloride. The temperature of 0° was maintained by an ice–salt-bath. The reaction showed the same color changes as the reaction at −80°, was hydrolyzed, and a yellow precipitate was isolated. The precipitate was recrystallized from toluene yielding 2.30 g. of a substance melting at 258° (compound A). After separation from the water layer, the ether was distilled away, and 0.9 g. (8.3%) of triphenylvinyl benzoate was obtained upon recrystallization. The mother liquors were condensed to yield 2.9 g. (36.8%) of triphenylvinyl alcohol.

Compound A.—The compound was dissolved in methyl alcohol and refluxed 48 hours with 10% alcoholic potassium hydroxide solution. A compound melting at 146° was obtained from the water layer and identified as diphenylacetic acid by a mixed melting point determination. **Diphenylmethane**, m.p. 24–26°, was recovered from the ether layer and identified as its nitro derivative.

The polymer of diphenylketene,[11] m.p. 244–245°, showed a melting point depression of thirty degrees with compound A. The analytical data for compound A suggest the single addition of phenyllithium to the dimer of diphenylketene followed by the usual reaction with benzoyl chloride to give a compound with a formula of $C_{41}H_{30}O_3$.

Anal. Calcd. for $C_{41}H_{30}O_3$: C, 86.29; H, 5.29; mol. wt., 571. Found: C, 87.45, 87.21; H, 5.14, 5.36; mol. wt., 608, 647.

Addition of Phenyllithium to Diphenylketene at 20°.—The procedure described above was repeated with 0.036 mole of phenyllithium and 0.034 mole of diphenylketene at a bath temperature of 20° with subsequent addition of benzoyl chloride. After hydrolysis the ether was removed by distillation. On recrystallization from alcohol the residue yielded 4.6 g. of a substance melting at 175° (compound B).

Compound B.—The compound was refluxed in a 10% alcoholic potassium hydroxide solution for 24 hours. From the saponification mixture, benzoic acid and diphenylmethane were isolated and identified.

The analytical data indicate that compound B may possibly be a nine-molecule polymerization product of diphenylketene, $(C_{14}H_{10}O)_9$.

Anal. Calcd. for $(C_{14}H_{10}O)_9$: C, 86.57; H, 5.19; mol. wt., 1748. Found: C, 86.65, 86.57; H, 5.38, 5.22; mol. wt., 1773, 1808.

Addition of Diphenylketene to Phenyllithium at 20°.—To a solution of 0.06 mole of phenyllithium in ether was added 11.0 g. (0.057 mole) of diphenylketene in ether. Approximately one-half hour after the addition was complete 8.5 g. (0.07 mole) of benzoyl chloride was added to the mixture. On working up in the manner described above an 86.4% yield of triphenylvinyl benzoate (m.p. 151°) was obtained.

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Note on the Theory of the Kinetics of Polarographic Electrode Processes

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In the last few years increased attention is being paid to polarographic electrode processes involving various reactions the rate of which, jointly with the diffusion of reactants, controls the resulting depolarization current. The contributions to this problem concern on the one hand reactions occurring in the solution surrounding the electrode, and on the other hand processes related to the electron exchange with the depolarizer. Since the investigations of this problem are being developed in different laboratories and its original treatment is not always adequately referred to, interpreted or known, we wish to present here some comments on this subject.

In the first attempt[1–3] to define the kinetic component of the total limiting current, the concept of a reaction layer around the electrode was introduced. Instead of considering the transfer of the reactants from the bulk to the electrode, their concentrations at the surface of the electrode were expressed with the Ilkovič diffusion formula. This simplified treatment of the problem was completed by Wiesner[4] with a statistical estimate of the effective thickness of the reaction layer made on the basis of the Einstein–Smoluchowski law.

The first treatment of the problem using a system of differential equations with appropriate boundary conditions describing the diffusion to a plane electrode and considering the reversible formation of the depolarizer in the solution, was worked out by Koutecký and Brdička.[5] The results were extended with certain approximations to the dropping electrode and tabulated data were furnished for an easy evaluation of the rate constants due to ionic recombination of weak acids from the limiting currents observed. Small but distinct deviations of the theoretical results from the experimental data were ascertained concerning the variation of the limiting currents with the *p*H and the drop time,[6] the theoretical curve being somewhat steeper than the experimental one. It was shown at the same time that the Wiesner statistical definition of the thickness of the reaction layer represents a reliable estimate, provided that the rates of recombination are high enough.

After extending this mode of procedure to various general schemes of electrode processes among which the problem of the regeneration of the depolarizer during the depolarization process was also discussed,[7] a more accurate treatment of the rate-controlled currents was recently presented by Koutecký[8,9] in which the growth of the dropping electrode against the electrolyte was taken into account. With this essential improvement the theoretical results fully agree with the experimental

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[3] R. Brdička and K. Wiesner, *ibid.*, **12**, 138 (1947).

[4] K. Wiesner, *Chem. Listy*, **41**, 6 (1947).

[5] J. Koutecký and R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 237 (1947).

[6] V. Hanuš, *Proc. Intern. Polarog. Congr. Prague*, Part I, 803 (1951).

[7] J. Koutecký, *ibid.*, Part I, 826 (1951); *Chem. Listy*, **46**, 193 (1952); *Collection Czechoslov. Chem. Communs.*, **18**, 183 (1953).

[8] J. Koutecký, *Chem. Listy*, **47**, 9 (1953); *Collection Czechoslov. Chem. Communs.*, **18**, 311 (1953).

[9] J. Koutecký, *Chem. Listy*, **47**, 323 (1953); *Collection Czechoslov. Chem. Communs.*, **18**, 597 (1953).

data, from which reliable values of the rate constants are obtained.[10-12]

Since 1951 Delahay and his co-workers have published in THIS JOURNAL a series of papers dealing with the same or similar questions. In the course of their work the authors have gradually approached the results[13,14] which in a more general form were already obtained in 1947. The apparently simplified treatment of the recombination process suggested by Delahay[13] is similar to that also discussed in our paper (*cf.* ref. 5, p. 350). Though this paper is mentioned by Delahay, the meaning of the heterogeneous rate constant used in his treatment is obviously misunderstood. Whilst it is true that the heterogeneous constant can be defined as the product of the thickness of this layer and of the rate constant of recombination, the thickness of this layer is by no means related to the distance between two molecules of the reacting substance in the solution. This erroneous assumption regarding the thickness of the reaction layer led Delahay even in his later publications[14-16] to a false computation of the rate and the equilibrium constants for the ring-aldehydo transformations of various aldoses.[14] With proper treatment the rate constants cannot be evaluated unless the respective equilibrium constants are known from other measurements (*cf. e.g.*, the rate of dehydration of formaldehyde[17]).

The treatment by Delahay and Stiehl[18] of catalytic currents observed at the electro-reduction of ferric ions in the presence of hydrogen peroxide and strictly valid only for a plane electrode, is included, as mentioned above, in the solution of the general schemes worked out by Koutecký.[7] Its application to this special case was discussed in detail by Pospíšil.[19] Its solution by Miller[20] represents an improvement since it distinguishes the effect of the growth of the electrode on the kinetic and diffusion component of the limiting current by introducing an empirical factor for the kinetic component. This effect was exactly allowed for first by Koutecký[8] and verified by Pospíšil,[19] Blažek and Koryta[11] and Koutecký, Brdička and Hanuš.[12]

As far as the processes due to the "slow electron transfer" are concerned, the first solution of this problem considering the mass transfer to the plane electrode was given by Smutek,[21] Delahay and Strassner,[22] Evans and Hush[23] and Kambara and Tachi.[24] Later on Delahay[25] presented the results in a more comprehensive form giving useful criteria for the shapes of irreversible waves. However, the former computations of Delahay and Strassner[22] applied to the iodate ions are dubious, since the authors do not consider the fact that owing to the recombination of the iodate ion with hydronium ions a complex wave is obtained.[26] The polarographic problem of the "slow electron transfer" respecting the growth of the dropping electrode against the electrolyte was rigorously treated by Mejman[27] for the case of the one-way electron process. The extension to an electron transfer both ways has been worked out recently by Koutecký.[9] Discussion of the methods concerning the evaluation of the rate constants involved in the polarographic electrode process is the subject of a recent communication.[28]

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(+)α-Phenethyl Chloride and (−)2-Phenylpentane[1]

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This note describes experiments which place upper and lower limits upon the rotation of optically active α-phenethyl chloride *via* conversion of α-phenethyl alcohol to the chloride and *via* conversion of the chloride to 2-phenylpentane. It also describes a preparation of α-phenethyl chloride of high rotation in much improved yield.

Gerrard[2] has described a preparation of the chloride employing pyridine and phosphorus oxychloride which gives much larger rotations than methods previously employed. We have confirmed these results and obtained a chloride the rotation of which very slightly exceeded the highest reported by Gerrard. This establishes a lower limit to $\alpha^{25}\text{D}$ of 109°.

Employing the Letsinger[3] modification of the Wurtz reaction, optically active α-phenethyl chloride was converted to 4-phenyl-1-pentene by reaction with allylsodium. This was hydrogenated to 2-phenylpentane. From the ratio of the observed rotation of this material to that reported for the optically pure material by Cram,[4] the upper limit to the rotation of α-phenethyl chloride is 126°. No assignment can be made of the difference between 109° and 126° as to loss of optical purity in forming the chloride from the alcohol and in forming the olefin from the chloride. It is unlikely

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(1) The first two authors wish to express their thanks to the Office of Naval Research for the support of their research.

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