Scheme I

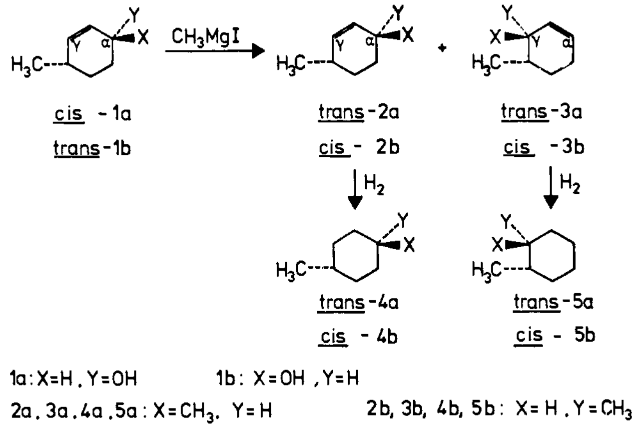
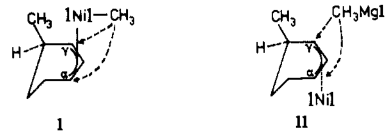


Table I. Isomeric Product Composition in the Alkylation of *cis*- (**1a**) and *trans*-4-Methyl-2-cyclohexen-1-ol (**1b**)

starting product (diastereomeric purity, %)	isomeric product composition, %			
	trans-**2a**	*trans*-**3a**	*cis*-**2b**	*cis*-**3b**
cis-**1a** (99)	52.5	46.5	1	0
trans-**1b** (98)	1	1	88	10

Chart I. Possible Intermediates in the Alkylation of *trans*-**1b**



a matter of fact the ratio of α to γ attack is 1.1 for *cis*-**1a** and 8.8 for *trans*-**1b**.

Reasonable arguments have been presented that the nickel-catalyzed alkylation of allylic alcohols with Grignard reagents proceeds via a π-allylnickel intermediate.[8,9] Such an intermediate is further supported by the fact that in the enantiomer discriminating alkylation by methylmagnesium iodide of racemic 2-cyclohexen-1-ol[5] catalyzed by [(−)-(*R*)-1,2-bis(diphenylphosphino)-1-phenylethane]nickel(II) chloride, the optical purity of the recovered alcohol depends on the extent of conversion whereas that of the 3-methylcyclohexene formed does not.[10] With the assumption of a π-allyl intermediate, the observed stereochemistry can be the result of two different pathways: (i) formation of an allyl nickel intermediate with anti attack and alkyl transfer on the frontside of the π-allyl system with respect to the nickel atom (Chart I, I); (ii) formation of the π-allyl species with syn stereochemistry followed by exo attack of the Grignard reagent (Chart I, II). Both possibilities can account for the difference in regioselectivity (α:γ attack ratio) found in the alkylation of *cis*-**1a** and *trans*-**1b**. As a matter of fact, the attack at the γ position is sterically less favored than at the α position; this difference is even greater when the methyl group on the ring is syn rather than anti with respect to the incoming nucleophile. It is worthwhile to note that the same stereochemistry and similar regioselectivity have been found for the copper-catalyzed alkylation of allylic ethers by Grignard reagents.[11]

Work is in progress with the aim of isolating diastereomeric allyl nickel complexes related to the proposed intermediate and to distinguish if possibility i or ii is in effect.

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Stoichiometric Decarbonylation of Benzoyl Chloride by Chlorotris(triphenylphosphine)rhodium(I)[1]

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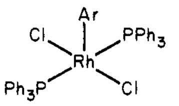
Some think that the stoichiometric (30–100 °C) and catalytic (~180 °C) decarbonylations of benzoyl chloride by $RhCl(PPh_3)_3$ proceed by comparable mechanisms to give the same products, chlorobenzene and $RhCl(CO)(PPh_3)_2$.[2] The difference between the stoichiometric and catalytic reactions is simply attributed to the lack of further reactivity of $RhCl(CO)(PPh_3)_2$ at low temperatures.[3] These views are based, in part, on a analogy to the decarbonylations of other nonaromatic acid chlorides and are summarized by Scheme I. In addition, there is a direct report[4] that $RhCl(PPh_3)_3$ reacts with benzoyl chloride in benzene (80 °C, 15 min) to give high yields of chlorobenzene and $RhCl(CO)(PPh_3)_2$ and a reported kinetic study[5] of the low-temperature decomposition of an isolated intermediate, $RhCl_2(CO)(Ph)(PPh_3)_2$ (**3a**), to give the same products. We now report that the stoichiometric decarbonylation of benzoyl chloride by $RhCl(PPh_3)_3$ at low temperatures does not give chlorobenzene; the aryl-containing product of the reaction is $RhCl_2(Ph)(PPh_3)_2$ (**5a**). The thermal decomposition of isolated $RhCl_2(CO)(Ph)(PPh_3)_2$ (**3a**), also gives the same complex **5a** and does not give chlorobenzene.



5a,b

The reaction of $RhCl(PPh_3)_3$ with excess benzoyl chloride for 15 min at 80 °C according to the literature procedure[4] gave a yellow precipitate which was readily identified as $RhCl_2(CO)(Ph)(PPh_3)_2$ (**3a**), identical in all respects to an authentic sample.[5-7] Further workup of the filtrate[8a] showed that neither chlorobenzene[8b] nor $RhCl(CO)(PPh_3)_2$ (IR, 1968 cm^{-1}) had been formed.

Since $RhCl_2(CO)(Ph)(PPh_3)_2$ is thought[3,5] to be an intermediate on the path to chlorobenzene and $RhCl(CO)(PPh_3)_2$, the reaction described above was simply continued for longer reaction times (24–96 h). Alternatively, complex **3a** was isolated, purified, and reintroduced to a benzene solution of benzoyl chloride at 80 °C. These two experiments differ with respect to 1 equiv of free PPh_3

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(1) Taken, in part, from the Ph.D thesis of J. B. Philip, Jr., University of Rochester, NY, 1980.

(2) These reactions are cited in many textbooks and monographs: Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; pp 90–92. Heck, R. F., "Organotransition Metal Chemistry"; Academic Press: New York 1974; pp 264–265. The literature has been summarized and reviewed several times, most recently and thoroughly by Baird (Baird, M. C. In "The Chemistry of Acid Derivatives"; Patai, S., Ed., Wiley: New York, 1979; Supplement B, Part 2, pp 825–857. See also: Tsuji, J. In "Organic Synthesis by Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 595–654.

(3) We do not mean to specify, in detail, how $RhCl(CO)(PPh_3)_2$ reenters the cycle. Proposals range from a direct reaction with acid chloride[3a] to initial loss of phosphite[3b] to initial loss of CO.[3c] Others have proposed that $RCl(CO)(PPh_3)_2$ is not even involved.[3d] (a) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99–107. (b) Stille, J. K.; Huang, F.; Regan, M. T. *Ibid.* **1974**, *96*, 1518–1522. (c) Strohmeier, W.; Pföhler, P. *J. Organomet. Chem.* **1976**, *108*, 393–399. (d) Blum, J.; Oppenheimer, E.; Bergmann, E. D. *J. Am. Chem. Soc.* **1967**, *89*, 2338–2341.

(4) Blum, J. *Tetrahedron Lett.* **1966**, 1605–1608.

(5) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508–1514.

(6) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1347–1360.

(7) That is, mp, IR, ^1H NMR, and ^{31}P NMR. The IR absorption at 2070 cm^{-1} and the Rh–^{31}P coupling constant, $J = 88.5$ Hz, are diagnostic for Rh(III)–CO complexes. See: Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71–76.

(8) (a) The filtrate was separated into volatile and nonvolatile fractions by bulb-to-bulb distillation in vacuo and analyzed by gas chromatography and IR spectroscopy, respectively. (b) A 1% yield was readily detectable by GC.

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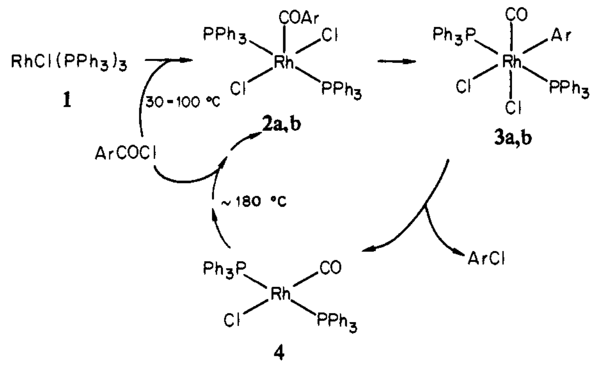
Scheme I. Proposed Sequence for the Stoichiometric and Catalytic Decarbonylations of Aroyl Chlorides

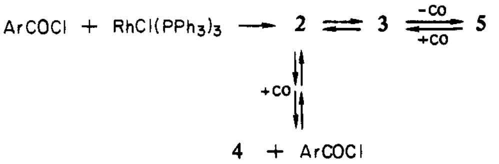


a, Ar = C_6H_5; b, Ar = p-$CH_3C_6H_4$

liberated from $RhCl(PPh_3)_3$; free PPh_3 is reported[5] to inhibit the decomposition of **3a**. In any case, both experiments gave similar results. Complex **3a** disappeared slowly to give a mixture of $RhCl(CO)(PPh_3)_2$ (**4**), and $RhCl_2(Ph)(PPh_3)_2$ (**5a**); chlorobenzene was not formed. The mixture of **4** and **5a** can be separated by chromatography on silica gel to give the pure components.[9-11] The mixture can also be analyzed by comparing the absorbances at 1968 (**4**) and 340 cm^{-1} (**5a**) to a working curve constructed from absorption data for authentic mixtures of the pure components. Complex **5a** was always the major rhodium-containing product in these experiments in the presence of excess acid chloride (i.e., **5a**/**4** $\gg$ 1). Comparable results were obtained when these experiments were run in 1,2-dichloroethane (83 °C) or toluene (111 °C), under air or nitrogen, or if $RhCl(PPh_3)_3$ was reacted with p-methylbenzoyl chloride. The latter experiment is particularly revealing because the ^{1}H NMR spectrum of the mixture of rhodium complexes, **4**/**5b**, immediately shows that the p-tolyl group (δ 2.22) is still associated with the rhodium fraction.[12]

Carbon monoxide is evolved in these experiments. $RhCl(PPh_3)_3$ was reacted with excess p-methylbenzoyl chloride for 5 h in toluene at 111 °C to give a 70% yield of **5b** and a 10% yield of **4**. The evolved CO was entrained in a N_2 sweep and bubbled into an external solution of $RhCl(PPh_3)_3$ in $CHCl_3$ to give a 63% yield of $RhCl(CO)(PPh_3)_2$. A control experiment involving a N_2 sweep of a solution of $RhCl(CO)(PPh_3)_2$ in toluene at 111 °C for 5 h showed that this complex was unchanged (91% recovery) and did not evolve CO.

Scheme II



The reaction of equimolar amounts of $RhCl(PPh_3)_3$ with p-methylbenzoyl chloride in 1,2-dichloroethane at 83 °C under N_2 for 24 h gave complexes **5b** and **4** in about 1:1 ratio (55% and 42% yield, respectively.[13] p-Methylbenzoyl chloride was present at the end of the reaction as judged by IR absorptions at 1775 and 1730 cm^{-1}. A bulb-to-bulb distillation of the volatiles followed by hydrolysis led to the isolation of benzoic acid in 57% yield. This p-methylbenzoyl chloride is not *unreacted* starting material because the reaction of the acid chloride with $RhCl(PPh_3)_3$ to give complexes **2b** and **3b** is complete[5,6] in minutes at 83 °C. In addition, when a mixture of $RhCl_2(p\text{-toluoyl})(PPh_3)_2$ (**2b**) and $RhCl_2(CO)(p\text{-tolyl})(PPh_3)_2$ (**3b**) was isolated and independently thermolyzed in 1,2-dichloroethane at 83 °C, **4**, **5b**, and p-methylbenzoyl chloride was isolated in ~1:1:1 molar ratio; neither of these experiments[14] gave p-chlorotoluene[8b,14] or p-tolyltriphenylphosphonium chloride.[14] Both of these experiments indicate that the thermal decomposition of **3b** is not a simple reductive elimination to give ArCl + **4**; rather, a more complex set of reactions takes place to give **4**, **5b**, and starting acid chloride.

Complex **5b** reacted with CO in $CHCl_3$ at -10 °C for 24 h to give $RhCl_2(p\text{-toluoyl})(PPh_3)_2$ (**2b**) in 76% isolated yield, identical to an authentic sample.[5] The same reactants in CH_2Cl_2 at 25 °C gave $RhCl(CO)(PPh_3)_2$ (**4**) in 81% isolated yield. The solution showed IR absorptions at 1775 and 1730 cm^{-1} assigned to p-methylbenzoyl chloride; after deliberate hydrolysis, p-methylbenzoic acid was isolated in 99% yield.

These experiments on the decarbonylation reaction, the thermal decomposition of **3a,b**, and on the reactions of isolated complex **5b** with CO are complementary and are summarized in Scheme II. The source of the $RhCl(CO)(PPh_3)_2$ is not the reductive elimination of ArCl from **3**. As shown in Scheme II, there is no direct connection between **3** and **4** under these conditions. Rather, complex **3** loses CO to give **5**; this free CO then "back" reacts[15] with **2** to regenerate aroyl chloride and to form **4**. The final distribution of rhodium complexes between **5** and **4** in any given experiment will depend on a number of factors such as the rate of escape of CO from the system and the rate of the reaction of **4** with aroyl chloride.

Finally, it is clear that none of these intermediates (**2**, **3**, and **5**) decomposes to aryl chloride at low temperature. There is, however, a high-temperature catalytic reaction which really does give aryl chloride.[2,16] The experiments reported in this paper demonstrate that the chemistry of these stoichiometric decarbonylations of aroyl chlorides was incorrectly identified in the earlier

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(9) An equal weight of triphenylphosphine was added to a solution of the mixture of **4** and **5** in CH_2Cl_2 and the mixture chromatographed on silica gel with CH_2Cl_2 as the eluant. The addition of phosphine improved the recovery of **5** from the column. The ^{31}P spectrum of the mixture of **4** and **5** before chromatography was the simple composite of the spectra of the pure components after chromatography. Therefore, no change takes place during this separation procedure.

(10) **5a**, Anal. Calcd for $C_{42}H_{35}Cl_2P_2Rh$: C, 65.04; H, 4.56; P, 7.99; M_r 775. Found: C, 64.84; H, 4.66; P, 7.30; M_r (in CH_2Cl_2) 770. **5b**, Calcd for $C_{43}H_{37}Cl_2P_2Rh$: C, 65.42; H, 4.73; Cl, 8.98. Found: C, 65.28; H, 4.92; Cl, 8.97. **5a**: ^{31}P NMR δ 18.5 relative to $(MeO)_3PO$ (d, J = 103.2 Hz); IR (KBr) 340 cm^{-1}. **5b**: ^{31}P NMR δ 18.1 (d, J = 103.5 Hz); ^{1}H NMR 2.22 (s, 3 H); IR 338 cm^{-1}. The ^{31}P doublet corresponds to equivalent phosphines; the Rh–Cl stretch in the IR corresponds to trans chlorines.[10a] The structure shown for **5** is analogous to that established by X ray for $RhCl_2(COCH_2CH_2Ph)(PPh_3)_2$.[10b] (a) Brookes, P. R.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1079–1084. (b) Egglestone, D. L.; Baird, M. C.; Lock, C. J. L.; Turner, G. *J. Chem. Soc., Dalton* Trans. **1977**, 1576.

(11) Complexes like **5** have been mentioned previously as participants in these reactions but were not characterized (see, ref 3a,d).

(12) We assumed that the discrepancy between the literature reports (see ref 4 and 5) and our experiments (no ArCl) was due to the presence of an unknown and unsuspected "promoter". We therefore examined the effect of additives, PPh_3, oxygen, HCl, $CuCl_2\cdot 2H_2O$, $(CuCl)_2$, photolysis, impure acid chloride, impure solvent, molar ratio of reactants, and absolute concentration of $RhCl(PPh_3)_3$. The experiments in oxygen saturated systems gave low yields of chlorobenzene, 4–7%, and a 63% yield of $[RhCl(O_2)(PPh_3)_2]_2$, identical by IR spectroscopy with an authentic sample of the known complex.[12a,b] A control showed that this oxygen complex does not react with benzoyl chloride at 111 °C in toluene for 72 h to give chlorobenzene. All of the other additives or variables failed to promote the formation of chlorobenzene. (a) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1966**, 129–130. (b) Bennett, M. J.; Donaldson, P. B. *J. Am. Chem. Soc.* **1971**, *93*, 3307–3308.

(13) These experiments gave small variable yields (1–9%) of toluene. Triphenylphosphine oxide was also formed and could be identified in the reaction mixtures, before workup, by ^{31}P NMR [δ 26.6 relative to $(MeO)_3PO$]. The source of triphenylphosphine oxide is not known.

(14) Controls showed that these products are stable to the reaction and workup conditions. A 5% yield of phosphonium salt would have been detected. Phosphonium salts are formed in reactions of α,β-unsaturated acid chlorides with $RhCl(PPh_3)_3$. Kampmeier, J. A.f Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. soc.*, in press.

(15) There is analogy for this reaction which presumably proceeds via $RhCl_2(CO)(COAr)(PPh_3)_2$. See: Ref 6 and Lau, K. S. Y.; Becker, Y.; Huang, F.f Baenziger, N.; Stille, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 5664–5672. We do not mean to distinguish between reaction of CO with the cis or trans isomers of **2**.

(16) Thermal decomposition of an isolated mixture[5] of **2b** and **3b** in o-xylene at 144 °C for 2.5 h gave a 14% yield of p-chlorotoluene. This same experiment, in the presence of excess p-methylbenzoyl chloride, gave a catalytic reaction; 44% of the starting aroyl chloride was coverted to aryl chloride. This conversion corresponded to the formation of 14 mol of p-chlorotoluene per mol of aded rhodium complexes.

studies. Thus, the tidy relationship between the stoichiometric and catalytic reactions, as outlined in Scheme I, is also incorrect. In particular, the immediate precursor and the route to chlorobenzene in the catalytic reaction remain to be identified.

Acknowledgment. This work was supported, in part, by the National Science Foundation, NSF 7308798. We appreciate a generous loan of $RhCl_3$ from Matthey-Johnson, Inc., and important discussions with Professor Richard Eisenberg.

Stabilization of n-Type Silicon Photoelectrodes to Surface Oxidation in Aqueous Electrolyte Solution and Mediation of Oxidation Reaction by Surface-Attached Organic Conducting Polymer

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A major impediment to the exploitation of photoelectrochemical cells in solar energy conversion and storage is the susceptibility of small bandgap semiconductor materials to photoanodic and photocathodic degradation.[1-3] We have found that the photoanodic degradation of n-type Si can be greatly suppressed in aqueous solution by electrodeposition of an organic conducting polymer (polypyrrole) on the surface of the electrode. The conducting polypyrrole film protects the n-type Si electrode against SiO_2 formation, presumably by covering potential oxide-forming sites and efficiently directing photoinduced charge in the semiconductor across the film before the charge has an opportunity to react with the semiconductor electrode. These effects are similar to those reported[4] for n-type Si derivatized with ferrocene complexes, but the nature of the modified surface is quite different. The degree of stability produced and the ease of film deposition are quite remarkable and provide encouragement for the potential application of organic conducting polymer films to practical photoelectrochemical devices for solar energy conversion.

Previous work[5] on n-type GaAs coated with polypyrrole also shows stabilization of the semiconductor against photocorrosion; however, the polymer film exhibited poor adhesion in aqueous electrolyte. Other interesting papers have been published on the nature of polypyrrole-coated metal electrodes; electrochemical synthesis of polypyrrole having conductivities in the range of 10–100 Ω^{-1} cm^{-1} on platinum electrodes have been reported.[6] We have carried out photoelectrochemical studies of polypyrrole deposited on n-type crystalline and polycrystalline Si in aqueous solution. The photoelectrochemical behavior of the crystalline and polycrystalline materials are similar, although the surface treatment and morphology of the electrodes necessary to form the film may differ. In this communication we shall report results only on the n-type polycrystalline Si.

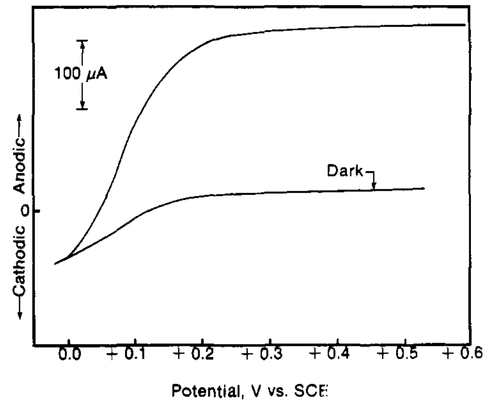

Figure 1. Current–potential curves (50 mV/s) of polypyrrole-covered polycrystalline n-type Si electrode in the dark and in the light in 0.15 M $FeSO_4$, 0.15 M $FeNH_4(SO_4)_2 \cdot 12H_2O$ and 0.1 M Na_2SO_4 in water at pH 1 under He at 295 K. Illuminated with tungsten–halogen light at 87 mW/cm^2.

The polypyrrole films were synthesized potentiostatically under illumination on the n-type silicon surfaces in a three-electrode, three-compartment cell containing 1.0 M pyrrole and 0.3 M tetraethylammonium fluoroborate in a helium-bubbled acetonitrile solvent which was stirred mechanically.

Electrodes were fabricated from polycrystalline n-type Si (20–30-Ω-cm resistivity) with a grain size of about 1.5 mm × 4 mm. Ohmic contacts were made with an alloy solder of 10% silver and 90% indium. The wire leads were encased in a glass tube for mounting and insulated with epoxy to expose only the Si surface. The electrodes were etched for 10 s in concentrated HF at room temperature immediately prior to electrodeposition of the polypyrrole film. Deposition on n-type Si begins ca 0.45 V vs SCE under illumination (ca. 200 mW/cm^2) with a tungsten–halogen lamp. Films were formed at constant potential at voltages between 0.6 and 0.9 V. During the synthesis, the current remained practically constant at 100 $\mu A/cm^2$. On the basis of charge density passed (between 1 and 10 mC/cm^2), and assuming 2.2 F mol^{-1} of pyrrole,[6] the films typically were 140–1200-Å thick. Illumination of the electrodes was carried out with a 100- or a 250-W tungsten–halogen lamp; unless otherwise noted, the radiation was unfiltered.

Polypyrrole-covered n-type Si was characterized by cyclic voltammetry in 0.15 M $FeSO_4$, 0.15 M $FeNH_4(SO_4)_2 \cdot 12H_2O$, and 0.1 M Na_2SO_4 in aqueous solvent at pH 1. Figure 1 shows the current–potential characteristics of polypyrrole-covered n-type Si in the dark and under illumination. The polypyrrole-covered electrode exhibits typical n-type behavior. The oxidation wave of the coated electrode is strongly dependent on the incident light intensity, whereas the cathodic current is relatively unaffected by light. The onset potential of the photoanodic current corresponds to the flatband potential of n-type Si (ca. 0.1 V), which was determined independently by capacitance measurements. The current–potential data in Figure 1 are the average of ca. 50 scans at 50 mV/s; little difference was observed between the first and last scan. In marked contrast, the photoanodic current of the naked (film-free) n-type Si electrodes diminishes rapidly to nearly zero after 1–2 scans.

The power characteristic of a polypyrrole-covered n-type Si electrode in an iron sulfate solution of the same composition referred to above was examined under nonoptimal conditions (i.e., with respect to the separation distance between the working and the counter electrodes, the potential of the redox couple, the electroyte concentration, etc.) and with no IR compensation. The electrode was illuminated with a tungsten–halogen lamp that delivered 24.5 mW/cm^2; this radiant power has been corrected for the infrared absorption (mainly, $\lambda \geq 1200$ nm) of a 4-cm length water filter and absorption due to the electrolyte solution. The power conversion efficiency of the cell was 3%, corresponding to a short-circuit current of 2.9 mA/cm^2, an open-circuit voltage of 0.39 V, and a fill factor of 0.6. This efficiency can be compared

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