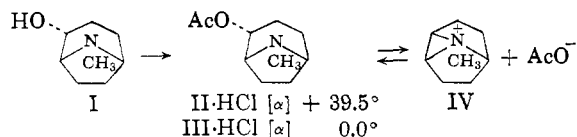(Nujol) of II·HCl, III·HCl and the crude mixture of hydrochlorides were identical.

We believe that the racemization proceeds through the intermediacy of the symmetrical ion IV

HO·⟨N-CH₃⟩ → AcO·⟨N-CH₃⟩ ⇌ ⟨N⁺-CH₃⟩ + AcO⁻

I   II·HCl [α] + 39.5°   IV
             III·HCl [α]   0.0°

The reverse reaction, the attack on IV by acetate ion, occurs with inversion to give III.

L(−)-2β-Tropanol afforded L(+)-2β-tropanyl acetate (hydrochloride[2] m.p. 219–222°, [α]^{25}D +3.5° (2.5% H_2O)) in high yield when refluxed for three hours with acetic anhydride. The "wrong" stereochemistry of this isomeric alcohol precludes the formation of the ion IV.[3]

(3) The rates of racemization and ionization of 2-tropanol derivatives are being studied in another laboratory; private communication from Prof. H. L. Goering.

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A NEW TECHNIQUE FOR THE DIRECT STUDY OF REACTANT ADSORPTION AT PLATINUM ELECTRODES

Sir:

Adsorption of reactants on mercury and platinum electrodes frequently has been proposed as a likely step in the kinetics of electrode reactions.[1,2,3,4] Usually the presence of adsorption has been inferred from experiments that also involved the reaction of the unadsorbed reactant dissolved in the body of the solution. Commonly, when the bulk concentration of the reactant is large enough to produce appreciable adsorption on the electrode, almost all of the current in electrochemical experiments results from the reaction of the unadsorbed reactant at the electrode, so that the interpretation of the experimental results is difficult and no direct information on the nature of the adsorbed species is obtained.

Lorenz[5] has resorted to the use of platinized platinum electrodes to increase the proportion of the current corresponding to adsorbed reactants. However, platinization of the electrode often leads to larger and undesirable contributions to the current from the charging of the double layer and this leads to experimental difficulties.

We have found recently that a number of reactants of electrochemical interest remain adsorbed on platinum electrodes for 10 to 20 minutes even when the electrode is removed from the reactant

(1) H. Matsuda and P. Delahay. Collection Czechoslov. Chem. Commun., 12, 2977 (1960).

(2) H. A. Laitinen and J. E. B. Randles, Trans. Faraday Soc., 51, 54 (1955).

(3) P. Delahay and I. Trachtenberg, J. Am. Chem. Soc., 80, 2094 (1958).

(4) A. Frumkin, Abstract No. 172, Electrochem. Soc. Meeting, Philadelphia, 1959.

(5) W. Lorenz and H. Mühlberg, Z. Elektrochem., 59, 730, 736 (1955).

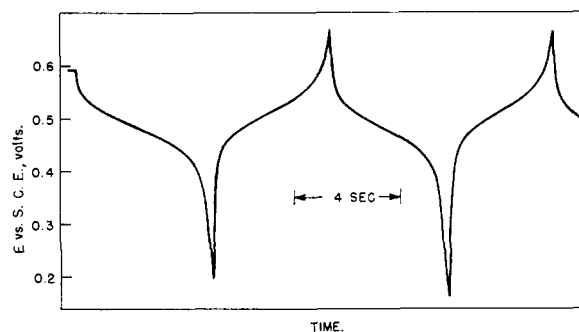solution and immersed in solutions free of dissolved reactant. This slow rate of desorption may be taken advantage of to study the adsorbed reactants under much to be preferred conditions where the only reaction going on at the electrode is due to the adsorbed reactant.

Chronopotentiometry[6] is ideally suited to the study of adsorbed reactants because experiments can be carried out rapidly compared to the rate of desorption in reactant free solutions. Figure 1 shows a set of chronopotentiograms for Fe(III) and Fe(II) adsorbed on a 0.1-cm.² platinum electrode, in which the direction of the current was reversed at each successive transition time. These chronopotentiograms were obtained by immersing the electrode in a solution 0.85 F in Fe(ClO₄)₃ in 1 F HClO₄ for 50 seconds, removing the electrode, washing it thoroughly with distilled water, placing it in the chronopotentiometric cell containing oxygen-free 1 F HClO₄, and recording the chronopotentiograms.

As would be expected for adsorbed reactants, the chronopotentiograms in Fig. 1 are completely unaffected by whether or not the solution is stirred during their recording. Furthermore the ratios of the cathodic to anodic transition times are approximately unity rather than one-third, the value obtained in the case of diffusion-controlled chronopotentiograms.[6] This observation shows that the Fe(II) produced by the reduction of Fe(III) remains adsorbed on the electrode.

Conclusive proof that these chronopotentiograms result from adsorbed Fe(III) and Fe(II) is obtained by comparing the observed chronopotentiograms with the theoretical equation for a chronopotentiogram from adsorbed reactants. In the case of a reversible diffusion-controlled chronopotentiogram for the reduction of Fe(III) the equation of the wave is[6]

$$E = E_{1/4} - \frac{0.059}{n} \log \frac{t^{1/2}}{\tau^{1/2} - t^{1/2}} \tag{1}$$

where E is the electrode potential, $E_{1/4}$ is E when $t = \tau/4$, τ is the transition time, and t is time. The corresponding equation in the case of an adsorption chronopotentiogram is

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{t}{\tau - t} \tag{2}$$

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Ch. 8.

Here $E_{1/2}$ is E when $t = \tau/2$. A plot of E vs. log $t/(\tau - t)$ for a chronopotentiogram such as those in Fig. 1 gave a straight line with a slope of 0.063 volt. This compares favorably with the theoretical value of 0.059 volt.

The analysis of chronopotentiograms for adsorbed reactants by means of plots of E vs. log $t/(\tau - t)$ is of particular value in cases where more than one form of the adsorbed reactant is possible. For example, cathodic chronopotentiograms for iodine adsorbed on a platinum electrode would obey the equation (3) if the iodine were present on the electrode as iodine molecules

$$E = E' - \frac{0.059}{2} \log \frac{t^2}{\tau - t} \qquad (3)$$

But the chronopotentiograms would obey equation 2 if the adsorbed iodine were present as iodine atoms. Experimentally, chronopotentiograms for adsorbed iodine give straight lines with slopes near the theoretical value for plots according to equation 2 but not with equation 3. Thus it may be concluded tentatively that iodine adsorbed on platinum electrodes is present as atomic iodine.

The extension of this technique should provide much useful information on the nature of reactants adsorbed on electrodes. It may even be possible to determine directly the contribution of adsorbed reactants to exchange currents measured in solutions of the reactants by performing rapid galvanostatic experiments with electrodes containing adsorbed reactants in separate, reactant-free solutions.

Further studies of this technique and its application to the examination of adsorbed Fe(II), Fe(III), I_2 and I^- are in progress and will be reported later.

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BICOÖRDINATE PHOSPHORUS: BASE-PCF₃ ADDUCTS[1]

Sir:

The cyclopolyphosphines $(PCF_3)_4$ and $(PCF_3)_5$[2] react easily and reversibly with trimethylphosphine or trimethylamine to form $(CH_3)_3PPCF_3$ or $(CH)_3$-$NPCF_3$. These evidently employ the PCF_3 unit in the same role as the $=O$, $=NH$, and $=CH_2$ units in the system of analogous R_3P and R_3N compounds discussed by Wittig and Rieber,[3] with the interesting difference that the PCF_3 complexes at room temperature easily dissociate to the tertiary base and $(PCF_3)_4$ and ₅, thus offering a way to improve the chemical availability of the PCF_3 unit.

(1) This research was supported by the United States Air Force under successive subcontracts of Prime Contracts AF 33(616)-5435 and 6913, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(3) G. Wittig and M. Rieber, *Ann.*, **562**, 181 (1949).

It is also interesting that the R_3PPCF_3 compounds are isomers of the diphosphines R_2PPR_2, and represent the first authentic examples of bicoördinate phosphorus in neutral molecules.

Formation of the Trimethylphosphine Complex. —When 0.990 mmole of pure $(PCF_3)_4$ and 4.22 mmoles of $(CH_3)_3P$ in a closed tube were warmed slowly from $-196°$, combination occurred with transient appearance of a yellow liquid but ending with a white solid. Removal of the excess $(CH_3)_3P$ in high vacuum at $-45°$ left a residue containing $0.98(CH_3)_3P$ per PCF_3 unit. With the absorption of small measured portions of $(CH_3)_3P$ by $(PCF_3)_4$ (weighed sample) at constant temperature, constant pressure was observed except for a distinct rise as the combining ratio approached 1:1. With 114 mm. pressure of $(CH_3)_3P$ at $21°$ (1 hr.) the ratio in the solid phase reached $0.985(CH_3)_3P$ per PCF_3 unit, but decreased as a small side reaction fouled the mercury manometer.

The quickly reproducible dissociation pressures in the mid-range of composition were 12.0 mm. at $23°$ and 53 mm. at $43°$, determining the equation $\log P_{mm} = 11.276 - 3020/T$ (calcd. at $0°$, 1.69 mm.; obsd., 1.65). Defining K_{eq} as pressure in atm., this gives $\Delta F^0 = 13.82 - 0.0384\ T$ for the dissociation of the solid complex to gaseous $(CH_3)_3P$ and the slightly volatile mixture of $(PCF_3)_4$ and $(PCF_3)_5$. Complete dissociation could be accomplished by high-vacuum fractional condensation, with all of the $(CH_3)_3P$ passing a trap at $-78°$. The trapped-out $(PCF_3)_n$ compounds showed an average vapor-phase mol. wt. of 414, indicating six $(PCF_3)_4$ (solid) to one $(PCF_3)_5$ (liquid) in the equilibrium mixture.

Catalytic Reorganization of the Polyphosphines. —The reversible formation of the PCF_3 complex implied that $(CH_3)_3P$ would catalyze the interconversion of $(PCF_3)_4$ and $(PCF_3)_5$. In fact, a one mole-per cent. addition of $(CH_3)_3P$ to pure $(PCF_3)_5$ caused a 50% conversion to $(PCF_3)_4$ during 48 hr. at $25°$. Such a conversion previously had required heating to $260°$.[2] In solution in ether or hexane, the catalyst converts the tetramer mostly to the pentamer, but without solvent, the tetramer (m.p. $66°$) is strongly favored by its solid-state energy. Higher $(PCF_3)_n$ polymers[2] are not found in the equilibrium mixtures.

A possibly similar catalysis occurred during a very fast 90% conversion of the triphosphine H_2-$(PCF_3)_3$[2] to $(HPCF_3)_2$ and $(PCF_3)_n$ by a trace of $(CH_3)_3P$ at $25°$.

Solution Behavior of the Complex.—The nearly colorless solutions of $(PCF_3)_4$ in liquid $(CH_3)_3P$ show average mol. wt. values (by vapor-tension lowering at $0°$) at least 25% higher than expected for pure $(CH_3)_3PPCF_3$, even at PCF_3 concentrations as low as 0.7 mole per cent. Also, when the solutions are chilled suddenly to $-78°$ and the free $(CH_3)_3P$ is distilled off, the residues never contain more than 0.88 $(CH_3)_3P$ per PCF_3 unit. Thus in solution with much excess $(CH_3)_3P$ the complex $(CH_3)_3PPCF_3$ is less completely formed than in the solid with little excess $(CH_3)_3P$. Apparently the conversion of solid tetramer (or liquid pentamer) to solid $(CH_3)_3PPCF_3$ is favored by the greater