

In similar experiments carried out at reaction temperatures of 25° for 17 hr. and at 62–75° for 20 hr., there were obtained respective conversions of 34 and 52%. In both cases the secondary iodide was the exclusive isomer formed.

Reactions of Tetrafluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 47.5 g. (0.374 g. at.) of iodine, 18.4 g. (0.083 mole) of undistilled iodine pentafluoride, 1 g. of aluminum shavings and 1 g. of aluminum iodide was heated in a nitrogen atmosphere in a 300-cc. Monel autoclave while shaking for 2 hr. at 130–140°. The autoclave was cooled, opened, and charged with 3 g. (0.0102 mole) of 1,1,2-trichloro-2,2-difluoro-1-iodoethane.² The reactor was sealed, cooled in liquid nitrogen, evacuated, and charged by vacuum gaseous transfer with 55 g. (0.55 mole) of tetrafluoroethylene. The reaction mixture was shaken at room temperature overnight and then heated while shaking at 50° for 7 hr. On venting the autoclave, there was recovered by condensation in refrigerated receivers 11 g. of unreacted olefin. By distillation of the remaining products there was collected a total of 80 g. (78% conversion based on maximum theoretical iodine monofluoride) of C₂F₅I³ shown by v.l.p.c. and by its infrared spectrum to exceed 99% purity.

In a similar run carried out in the absence of CF₂ClCCl₂I at 20–25° there was obtained only a very small yield of C₂F₅I, the principal products being CF₄ and carbon (*caution*). From two other runs in the absence of CF₂ClCCl₂I carried out mainly at 0°, 90% of the olefin was recovered unreacted in one case with a small amount of C₂F₅I formed, while in the other case there was once again almost complete conversion of the tetrafluoroethylene to carbon and carbon tetrafluoride with only a small quantity of C₂F₅I detected.

Reaction of 1-Chloro-2,2-difluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of undistilled iodine pentafluoride, 2 g. of aluminum shavings and 2 g. of aluminum iodide was heated in a nitrogen atmosphere in a 300-cc. Monel autoclave while shaking for 2 hr. at 135–140°. The reactor was cooled in Dry Ice, evacuated, and 64 g. (0.649 mole) of 1-chloro-2,2-difluoroethylene was admitted to the autoclave by vacuum gaseous transfer. The autoclave was sealed and shaken overnight at room temperature. On venting the autoclave at atmospheric pressure, there was recovered 31 g. of unreacted olefin. The remaining liquid products from the autoclave were hydrolyzed in cold aqueous saturated sodium bisulfite solution made basic with potassium hydroxide. The resulting mixture was neutralized with additional potassium hydroxide solution. The lower organic layer was separated and dried with Drierite. There was thus obtained 65 g. of liquid product, b.p. 60–80° (mostly 79–80°), shown by v.l.p.c. to contain 90 mole % (48% conversion based on maximum theoretical IF) of substantially a single isomeric iodide b.p. (middlecut) 80°, *n*_D²⁰ 1.4304. From the similarity of its vapor infrared spectrum to those of CF₃CHClBr, CF₃CHClF and CF₃CHF₂I as well as the position of the absorption maximum in the ultraviolet spectrum taken in isoöctane which was at 275 m μ , the iodide was assigned the structure CF₃CHClI. Characteristic absorption bands in the infrared vapor spectrum of CF₃CHClI are at 7.66vs, 7.89vvs, 8.39vs, 8.61vs, 9.03vs, 11.6s, 12.5vs and 15.0s μ .

Anal. Calcd. for C₂HClF₃I: C, 9.84; H, 0.44; F, 23.39; I, 52.01. Found: C, 10.04; H, 0.31; F, 23.12; I, 52.17.

Reaction of Trifluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride, 2 g. of aluminum shavings and 2 g. of aluminum iodide was heated for 2 hours at 130° while shaking in a 300-cc. Monel autoclave. The reactor was cooled in liquid nitrogen, evacuated, and 62 g. (0.757 mole) of trifluoroethylene was admitted to the autoclave by vacuum gaseous transfer. The autoclave was shaken at room temperature for 16 hr. and at 70–83° for 15 hr.

By the isolation procedures previously described there was obtained from this reaction 15 g. of CF₃CHF₂I as the exclusive isomer. A pure sample of this iodide was obtained by preparative chromatography using a 2-meter Perkin–Elmer “B” column. The characteristic v.l.p.c. elution time ratio *t*₀/*t*_{CCl₄} at 50°, for this column was 0.57. The iodide CF₃CHF₂I, a colorless liquid, *n*_D²⁰ 1.3665, has the characteristic absorption bands in the infrared (vapor) spectrum at 7.35vs, 7.82vs, 8.09s, 8.30vvs, 8.85vs, 9.22vs, 11.60s and 14.4vs μ . The maximum in the ultraviolet spectrum of CF₃CHF₂I taken in isoöctane was at 262 m μ .

Anal. Calcd. for C₂HF₄I: C, 10.54; H, 0.44; F, 33.34; I, 55.68. Found: C, 10.20; H, 0.68; F, 33.19; I, 55.65.

It should be noted that the other possible IF adduct of trifluoroethylene, *i.e.*, CHF₂CF₂I, has been reported to have an ultraviolet maximum in light petroleum at 266 m μ .¹³

Reaction of 1,1-Difluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride, 2 g. of aluminum shavings and 2 g. of aluminum iodide was heated at 130–140° for 2 hours while shaking in a 300-cc. Monel autoclave. After cooling in liquid nitrogen, the autoclave was evacuated and 50.5 g. (0.790 mole) of 1,1-difluoroethylene was introduced by vacuum transfer. The autoclave was shaken at 0–12° for 18.5 hr. and at 50° for 3 hr. There was obtained from this reaction among other products a low yield of CF₃CH₂I which was separated by v.l.p.c. using a 2-meter Perkin–Elmer “B” column. The characteristic elution time ratio *t*₀/*t*_{CCl₄} at 75° was 0.67. The infrared spectrum of this iodide matched the spectra of samples of CF₃CH₂I prepared previously by iodide displacement on 2,2,2-trifluoroethyl tosylate¹⁴ and by the thermal reaction of 1,1-difluoroethylene with iodine.¹⁵

Acknowledgment.—We wish to thank Dr. Arnold H. Fainberg for the chromatographic and infrared data, Mr. Fred P. Curtis for technical assistance and Mr. Howard Francis and co-workers for elemental analyses and ultraviolet spectra.

(13) R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

(14) G. V. D. Tiers, H. A. Brown and T. S. Reid, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

(15) M. Hauptschein, A. H. Fainberg and M. Braid, *J. Org. Chem.*, **23**, 322 (1958); the principal infrared bands for CF₃CH₂I are given therein.

COMMUNICATIONS TO THE EDITOR

THE RACEMIZATION OF L(+)-2 α -TROPANOL

Sir:

When L(+)-2 α -tropanol (I)¹ was treated at room temperature with acetic anhydride containing a drop of perchloric acid the acetate II, isolated as the hydrochloride,² was formed ($[\alpha]_{D}^{25} + 39.5^{\circ}$

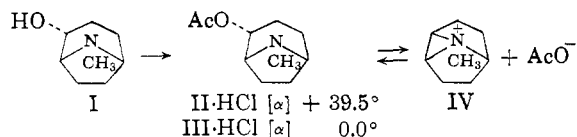
(2.5% H₂O)). When I was refluxed overnight with acetic anhydride the acetate III was obtained (hydrochloride, m.p. 195–197° $[\alpha]_{D}^{25} + 0.0^{\circ}$ (2.5% H₂O)). After three hours a mixture of II and III was formed from which a substantial amount of pure III·HCl was isolated. The infrared spectra

(2) Elementary analyses of all new compounds are satisfactory. Analyses and optical rotations were carried out under the supervision of M. E. Auerbach and F. C. Nashod, respectively.

(1) M. R. Bell and S. Archer, *J. Am. Chem. Soc.*, **82**, 4642 (1960).

(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



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

L(-)-2β-Tropanol afforded L(+)-2β-tropanyl acetate (hydrochloride² m.p. 219–222°, $[\alpha]_{\text{D}}^{25} +3.5^\circ$ (2.5% H₂O)) 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.

S. ARCHER
STERLING-WINTHROP RESEARCH INSTITUTE T. R. LEWIS
RENSSELAER, NEW YORK M. R. BELL

J. W. SCHULENBERG

RECEIVED APRIL 11, 1961

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.

Lorenz⁵ 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).

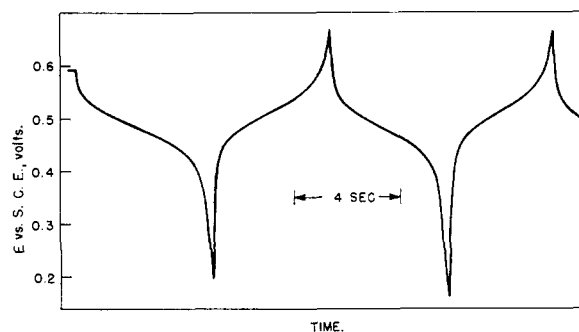


Fig. 1.—Alternate cathodic and anodic chronopotentiograms for Fe(III) adsorbed on the platinum electrode; current density was 100 microamperes per cm.².

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.

Chronopotentiometry⁶ 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 is⁶

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

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

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

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