*Russian Journal of General Chemistry, Vol. 73, No. 5, 2003, pp. 706–707. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 5, 2003, pp. 747–748.*
*Original Russian Text Copyright © 2003 by Tomilov, Kryukova, Martynov.*

# Conjugate Elimination of Fluorine Atoms in Halophosphonates

**A. P. Tomilov, E. V. Kryukova, and B. I. Martynov**

*State Research Institute of Organic Chemistry and Technology, Moscow, Russia*

Received April 2, 2001

**Abstract**—Facile electrochemical elimination of fluorine on a mercury drop electrode in aqueous-ethanol solutions on the background of 0.1 M $Bu_4NBF_4$ ($E_{1/2}$ 2.0 V against saturated calomel electrode) from diethyl chlorofluoromethyl- and diethyl dichlorofluoromethylphosphonates was observed. Under the same conditions, diethyl fluoromethylphosphonate is not reduced.

Halophosphonates are key starting materials for a number of physiologically active compounds. That is why their reactivity assessment presents considerable interest. One of the reactivity criteria for halogens in organic compounds is their polarographic reduction potentials. However, the information on the reduction potentials of halophosphonates is very scarce. The electrochemical reduction of diethyl trichloromethylphosphonate at a potential of –1.2 V was reported [1, 2]. The referees proposed that at this potential one chlorine atom is eliminated.

$$(EtO)_2P(O)CCl_3 \xrightarrow{2\bar{e}} (EtO)_2P(O)\bar{C}Cl_2 + Cl^-.$$

No $E_{1/2}$ values were presented.

In our study on electrochemical reduction of diethyl chlorofluoromethylphosphonate we observed selective reduction of chlorine, providing diethyl fluoromethylphosphonate in high yield, at a lead cathode potential of about –1.9 V. However, at a more negative cathode potential the yield of diethyl fluoromethylphosphonate decreased, presumably due to fluorine reduction. We thus had to assume that fluorine in this compound is electrochemically active. Since fluorine is known to be a hardly reduced element, we considered it of interest to study its polarographic behavior in halophosphonates.

The resulting reduction potentials are presented in the table. As seen from these data, diethyl fluoromethylphosphonate is inactive under the conditions studied. At the same time, the differential polarogram contains a well-defined peak at –2.03 V, assignable to fluorine elimination (see figure, curve *1*). Diethyl bromofluoromethylphosphonate gives one expected peak due to bromine reduction, and diethyl bromodifluoromethylphosphonate gives two peaks due to bromine and fluorine reduction. The behavior of phosphonates containing fluorine and chlorine proved unexpected. Inspite of the fact that they contain one fluorine atom in the molecule, a fluorine reduction peak was observed. The polarogram obtained for diethyl dichlorofluorophosphonate is presented in the figure (curve *2*). The first two peaks relate to successive elimination of chlorine, and the third one, to elimination of fluorine. Hence, the presence of chlorine activates the fluorine atom and facilitates its reduction at potentials more negative than 2.0 V. It is known that two halogen atoms at vicinal carbon atoms undergo facilitated conjugate elimination [4]. Such effect at the same carbon we observed for the first time and it deserves deeper investigation. However, the available evidence in insufficient for mechanistic conclusions concerning this phenomenon. Probably, the first electron transfer and C–X bond cleavage (X = F, Cl, Br) produces an unstable radical. The latter takes up a second electron at an appropriate potential, which induces C–F bond cleavage.

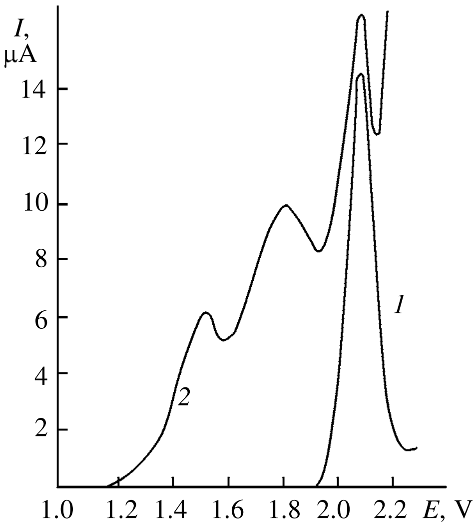
$$(EtO)_2P(O)CHXF \xrightarrow{\bar{e}} (EtO)_2P(O)\dot{C}HF \xrightarrow[-F^-]{3\bar{e},\ 2H^+} (EtO)_2P(O)CH_3.$$

It is possible that the wave at –0.2 V has a more

Reduction potentials of halophosphonates $(EtO)_2P(O)R$, $E_p$, V

| R | Bond cleaved | | |
|---|---|---|---|
| | C–Br | C–Cl | C–F |
| $CH_2F$ | – | – | – |
| CHBrF | –1.12 | – | – |
| $CHF_2$ | – | – | –2.03 |
| $CBrF_2$ | –0.95 | – | –2.02 |
| CHClF | – | –1.80 | –2.00 |
| $CCl_2F$ | – | –1.5, –1.72 | –2.05 |

1070-3632/03/7305-0706 $25.00 © 2003 MAIK “Nauka/Interperiodica”



Pulse polarogram of halogen-containing phosphonates in 0.1 M $Bu_4NBF_4$ in 50% ethanol. Potential scan rate 10 mV/s, pulse amplitude 25 mV, phoshonate concentration $10^{-3}$ M. (*1*) $(EtO)_2PCHF_2$ and (*2*) $(EtO)_2PCFCl_2$.

complex nature, but this question calls for further investigation.

## EXPERIMENTAL

The polarograms were obtained on a PA-2 pulse polarograph (Czech) in a three-electrode cell. The working electrode was a mercury drop electrode (dropping period 1 s). The auxiliary electrode was a platinum rod. The potentials were measured against an EVL-1M3 silver–silver chloride electrode. For more exact $E_{1/2}$ values, the measurements were carried out in the differential mode at the following conditions: pulse amplitude 25 mV, potential scan rate 10 mV/s. The background electrolyte was 0.1 M $Bu_4NBF_4$ in 50% aqueous ethanol. Before measurements the solution was purged with argon for 15 min. The halophosphonates used in this work were prepared by the Michaelis–Becker reaction by the procedure in [5].

## REFERENCES

1. Korrenbrock, F., Schafer, H., and Langer, I., *Tetrahedron Letters,* 1979, vol. 20, no. 31, pp. 2915–2916.
2. Tilborg, W., *Recl. Trav. Chim. Pays-Bas,* 1980, vol. 99, no. 6, pp. 202–206.
3. Tomilov, A.P., Martynov, B.I., Smirnov, Yu.D., and Semchenko, F.M., *J. Fluorine Chem.,* 1997, vol. 82, no. 1, pp. 39–41.
4. Tomilov, A.P., Fioshin, M.Ya., and Smirnov, B.A., *Elektrokhimicheskii sintez organicheskikh soedinenii* (Elektrochemical Synthesis of Organic Compounds), Leningrad: Khimiya, Khimiya, 1976, pp. 233, 243.
5. Grapov, A.F., *Reaktsii i metody issledovaniya organicheskikh soedinenii* (Reactions and Methods of Investigation of Organic Compounds), Kazanskii, B.A. and Knunyants, I.L., Eds., Moscow: Khimiya, 1966, vol. 15, p. 41.