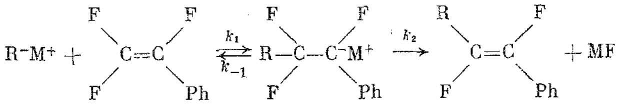
# IONS AND ION PAIRS OF ALKALI-METAL SALTS OF CH-ACIDS IN THE NUCLEOPHILIC VINYL SUBSTITUTION REACTION

A. A. Solov'yanov, M. M. Shtern,
I. P. Beletskaya, and O. A. Reutov

UDC 541.124.7:541.452

Despite the theoretical and practical importance of nucleophilic vinyl substitution reactions, for example, for the synthesis of vinyl compounds, few kinetic studies were made of such reactions [1]. Almost nothing is known regarding the reactivity of carbanions and the effects of ionic association in these processes. We studied the kinetics of the reaction between Li and Cs salts of certain CH-acids ($R^-M^+$) and $\alpha,\beta,\beta$-trifluorostyrene in dimethoxyethane at 25°C, and determined the rate constants of the reaction of free carbanions ($k_i$) and ionic pairs ($k_{ip}$) (see Table 1).

The reaction proceeds according to scheme (1) ($k_2 \gg k_1, k_{-1}$) and leads to a quantitative formation of the substitution product RFC=CFPh. For all the $R^-M^+$, the reactivity of the carbanion in the associated state is lower than in the free state ($k_{ip} < k_i$). Moreover, a clear correlation is observed in the change in $k_i$ in the substitution reactions at the saturated (in the reaction with $n$-$C_4H_9Br$) and unsaturated carbon atoms. The two factors indicate the determining role of the nucleophilicity factor in the reaction between $R^-M^+$ and $\alpha',\beta,\beta$-trifluorostyrene.



$$R^-M^+ + F_2C{=}CF(Ph) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R{-}CF_2{-}C^-F(Ph)\,M^+ \xrightarrow{k_2} RFC{=}CF(Ph) + MF \qquad (1)$$

TABLE 1

| CH-acid | $M^+$ | $k_i$ | $k_{ip}$ | $k_i$ ($n$-$C_4H_9Br$) [2, 3] |
|---|---|---|---|---|
| | | liter/mole · sec | | |
| Triphenylmethane | $Li^+$ | 400 | 46 | 903 |
| 9-Phenylfluorene | $Cs^+$ | 3,2 | $1{,}9 \cdot 10^{-2}$ | 0,22 |
| 1,3-diphenylindene | $Cs^+$ | 0,1 | $7{,}6 \cdot 10^{-3}$ | $1{,}4 \cdot 10^{-2}$ |
| 1,3-Diphenylindene | $Li^+$ | 0,1 | $3{,}0 \cdot 10^{-3}$ | $1{,}4 \cdot 10^{-2}$ |
| Fluoradene | $Li^+$ | $6{,}9 \cdot 10^{-2}$ | $3{,}4 \cdot 10^{-3}$ | $8{,}0 \cdot 10^{-3}$ |
| 9-Carbomethoxyfluorene | $Cs^+$ | $6{,}3 \cdot 10^{-3}$ | $6{,}4 \cdot 10^{-5}$ | $6{,}7 \cdot 10^{-3}$ |

## LITERATURE CITED

1. Z. Rappoport, Adv. Phys. Org. Chem., 7, 1 (1969).
2. A. A. Solov'yanov, I. P. Dem'yanov, I. P. Beletskaya, and O. A. Reutov, Zh. Org. Khim., 12, 2489 (1976).
3. A. A. Solov'yanov, A. D. Karpyuk, I. P. Beletskaya, and O. A. Reutov, Zh. Org. Khim., 17, 458 (1981).

---

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, p. 1673, July, 1982. Original article submitted March 10, 1982.

0568-5230/82/3107-1493$07.50