The α-Fluorine Effect and Carbanion Nucleophilicity

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Summary α-Fluoro-substituents destabilize sp^2-hybridized carbanions, thereby enhancing their nucleophilicity.

RECENT reports have shown both the kinetic[1,2] and the thermodynamic[3,4] acid-weakening effect of fluorine bonded to carbon bearing an acidic proton. If this is due to the instability of the α-fluorocarbanion relative to the unfluorinated carbanion, then the conjugate bases resulting from the dissociation of a proton from an acidic α-fluorocarbon should have enhanced nucleophilicity towards carbon. We report that this is so and give kinetic data for the first such observation of the α-fluorine effect on the formation of a carbon–carbon bond in the addition of substituted dinitromethide ions to the αβ-unsaturated system in methyl acrylate.

The Table shows values of the specific rate constant k_1 for the reaction:

$$\mathrm{RC(NO_2)_2^- + CH_2{=}CH{\cdot}CO_2Me \rightarrow RC(NO_2)_2{\cdot}CH_2\overset{-}{C}H{\cdot}CO_2Me}$$

With the exception of the fluorodinitromethide ion, the specific rates of addition of the remainder of the dinitromethide ion substrates are accommodated by a factor of 1·5. However, the substitution of fluorine for chlorine or an alkyl group enhances the nucleophilicity of the dinitromethide ion substrate so that fluorodinitromethide ion adds to methyl acrylate about 2000 times faster than the other dinitromethide ion substrates in either solvent system.

We have calculated activation parameters from the data in the Table and find the average values for the alkyl and chlorodinitromethide ions to be ΔH^* (50% dioxan) = 12·5 ± 0·1 and $\Delta H^*(\mathrm{H_2O})$ = 14·4 ± 0·1 kcal. mole^{-1} and ΔS^* (50% dioxan) = − 29·5 ± 0·4 and ΔS^* ($\mathrm{H_2O}$) = − 23·7 cal.deg.$^{-1}$. Since ΔS^* for the fluorodinitromethide ion, −30·4 ± 0·9 (50% dioxan) and −24·0 ± 1·3 ($\mathrm{H_2O}$) cal. deg.$^{-1}$, is essentially identical with ΔS^* (average) for the other substrates, the observed rate enhancement for the fluorodinitromethide ion is apparently not due to differences in the conformation of the ground state or of the transition state for fluorodinitromethide ion relative to the other dinitromethide ions. Large solvation differences between the fluorodinitromethide ion and its transition state relative to the other dinitromethide ions can be ruled out as being responsible for the observed rate enhancement for the fluorodinitromethide ion since $\Delta\Delta S^*$ and $\Delta\Delta H^*$ for this substrate in the above solvent systems is the same as the average value of these parameters, 5·8 cal. deg.$^{-1}$ and 1·9 kcal. mole^{-1}, for the other dinitromethide ion substrates. However, the magnitude of ΔH^* for the fluorodinitromethide ion, 7·4 ± 0·3 (50% dioxan) and 9·5 ± 0·4 (H_2O) kcal. mole^{-1}, is considerably smaller than is observed for the other dinitromethide ions.

TABLE

Specific rates of addition of substituted dinitromethide ions to methyl acrylate[a]

	50% Dioxan		Water	
R	10^4k_1 30°	10^4k_1 50°	10^4k_1 30°	10^4k_1 50°
Me	17·2 ± 0·0	67·1 ± 1·7	13·5 ± 0·1[b]	65·1[b]
Et	18·4 ± 0·2	70·7 ± 0·2	16·1 ± 0·5	75·5 ± 0·6
Cl	25·6 ± 0·4	98·5 ± 1·2	21·4 ± 0·3	100·9 ± 2·3
F	72·400[c]	164,000[c]	49,800 ± 1200	140,000[d]

[a] $\mu = 0{\cdot}1$, rate constants in M^{-1} sec.$^{-1}$.

[b] Data from S. S. Novikov, L. A. Nikonova, and V. I. Slovetskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1965, 1283.

[c] Calcd. from ΔH^* and ΔS^*, k_1 (25°) = 5·75 ± 0·08, k_1 (35°) = 8·89 ± 0·04.

[d] Calcd. from ΔH^* and ΔS^*, k_1 (15°) = 2·08 ± 0·05.

Therefore, the observed rate enhancement effected by the α-fluorine substituent must be due to destabilization of the ground state fluorodinitromethide ion. This is shown by a 5 kcal. mole^{-1} decrease in ΔH^* for the fluorodinitromethide ion. Explanations have been offered for the destabilizing effect of an α-fluorine substituent upon an sp^2-hybridized carbon atom which involve (a) weakening of the C–F σ-bond resulting from the increased electronegativity of an sp^2-hybridized carbon relative to an sp^3-hybridized carbon,[1] (b) repulsion of the delocalized *p*-electrons in the π-system of the carbanion by the *p*-pairs on fluorine.[5] Although no distinction as to which effect is operating to destabilize fluorodinitromethide ion can be made on the basis of the data presented, the magnitude of the α-fluorine effect should be proportional to the degree of planarity of the carbanion.

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