

Negative Hyperconjugation in Organic Fluorine Chemistry; Myth or Reality?

By JOHN H. SLEIGH, ROBERT STEPHENS, and JOHN COLIN TATLOW*

(Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT)

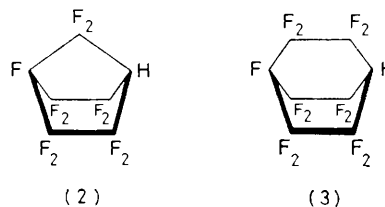
Summary New evidence from exchanges in neutral D_2O - CD_3COCD_3 , involving $(CF_3)_3CH$ and bridgehead compounds together, reopens an old controversy.

THE concept of negative hyperconjugation has long fascinated¹ all interested in organic fluorine chemistry. It has had distinguished protagonists,² and many have used it to explain aspects of reactivity for which simple inductive electron-attraction by fluorine seemed inadequate. Relative acid strengths of fluorocarbon hydrides were measured³ by base-catalysed deuterium uptakes and gave the order of acidity: $(CF_3)_3CH$ (**1**) $>$ $(CF_3)_2CFH$ $>$ $C_6F_{13}CF_2H$ $>$ CF_3H . Negative hyperconjugation was used³ to explain these results, the carbanion from the most acidic compound tris(trifluoromethyl)methane (**1**) having the greatest number of possible hyperconjugative contributors, *e.g.* $(CF_3)_2C=CF_2F^-$ (**1a**).

Subsequently, the concept has fallen into disrepute.¹ An authoritative review⁴ showed that many effects attributed to it could be explained otherwise, and acidity measurements,^{4,5} involving base-catalysed tritium exchanges on bridgehead compounds (**2**) and (**3**), synthesised^{6,7} by us, gave pK_a values lower than those calculated^{4,5} from the results³ on (**1**). Hyperconjugative contributors analogous to (**1a**) are extremely unlikely in bridgehead systems because of the usual 'Bredt's rule' considerations.⁸

Others,^{9,10} working with different types of compound, also rejected the postulate. The $I-\pi$ effect, widely used in organofluorine chemistry, is now the accepted explanation^{1,4,9-11} for these acidities.

Two issues worried us however: (a) results of polarographic measurements on mercurials derived from (**1**)¹² and (**2**)¹³ did not indicate comparable acidities (though the relationship of acidity to polarographic data is not fully proven); and (b) compounds (**1**), (**2**), and (**3**) had never been



compared with each other in the same system. The latter was not too easy to do, given the poor solubility characteristics of highly fluorinated compounds. Further, acyclic polyfluoro-compounds, and especially (**1**), lose HF quite readily in basic media,³ in fact not so much more slowly than they exchange H for D. In contrast, our bridgehead compounds, *e.g.* (**2**) and (**3**), are very resistant to olefin-

forming eliminations, giving bridgehead 'olefins'⁸ only under forcing conditions.^{6,7}

Following earlier observations,^{7b} we have now carried out simple deuterium exchanges in a neutral medium [$\text{CD}_3\text{-COCD}_3 + \text{D}_2\text{O}$ (9:1)] on mixtures of (1) + (2) together, and (1) + (3) together. The results are surprising. After 450 h at 50 °C in a sealed system, deuterium contents of the products isolated were measured by mass spectrometry as follows: from (1) over 70%, from (2) none detectable, from (3) 12%. Ratios of rate coefficients are k_1/k_3 ca. 10 and k_1/k_2 at least 60 and most probably > 100.

Several explanations may be offered: (i) these neutral reactions may be essentially $\text{S}_{\text{E}}2$ rather than $\text{S}_{\text{E}}1$ in character; (ii) solvent effects of some sort could badly distort the true situation; (iii) simple inductive effects may still explain the new results. However, none of these seems entirely satisfactory.

If apparently comparable acidities for (1), (2), and (3) were a strong argument against negative hyperconjugation,^{1,4,5a,14} the demonstration that, in these new exchanges, (1) reacts significantly faster than (2) (particularly) and (3), must now introduce doubts about the situation.

The question has to be reopened as to whether negative hyperconjugation could be, after all, a significant factor in organofluorine chemistry, at least as far as fluorocarbanions are concerned. Does it perhaps explain the ready loss of fluorine as fluoride ion from some perfluoroalkyl groups,^{2a} and particularly the ready dehydrofluorination³ of (1)? Both the $I-\pi$ effect and negative hyperconjugation were recently¹⁵ invoked, together, to explain the photoelectron spectrum of 1,1-difluoroallene.

We do not say that negative hyperconjugation is rehabilitated as a concept: just that, as happens in science, more work is now necessary to settle an issue thought to have been resolved.

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