ELIMINATION *VERSUS* DISPLACEMENT REACTIONS: AN ALTERNATIVE MECHANISTIC

INTERPRETATION OF 'THE ANOMALOUS REACTIONS OF F-PROPENE DIMERS WITH

THIOLATE IONS'
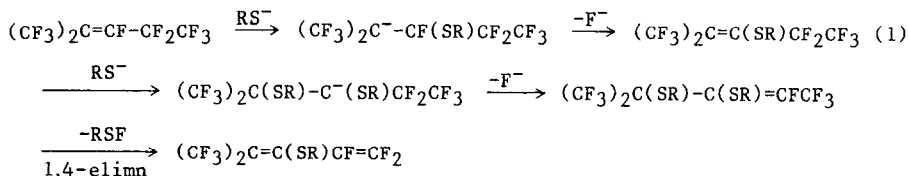
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SUMMARY

    In 1979 Ishikawa and Maruta reported experimental studies of the
reaction of two F-propene dimers, the F-2- and 4-methyl-2-pentenes with
thiolate ions. Highly unexpected products, the mercapto derivatives of
F-4-methyl-1,3-pentadiene, were isolated. These authors proposed a novel
mechanism which included the unprecedented 1,4-elimination of a sulfenyl
fluoride from a fluorinated thioether. In the current paper the
energetics of this reaction are explicitly discussed and an alternative,
more precedented, mechanism is offerred.

LITERATURE MECHANISM AND THERMOCHEMICAL ANALYSIS

    In 1979 Ishikawa and Maruta [1] reported experimental studies of the
reactions of the isomeric F-propene dimers, F-2- and 4-methyl-2-pentene,
with the highly nucleophilic $C_6H_5S^-$ and $C_6H_5CH_2S^-$ ions. Highly unexpected
products, the 3-mercapto derivatives of F-4-methyl-1,3-pentadiene, were
isolated in good yield. The following summarizes the literature
mechanism:

$$(CF_3)_2C=CF-CF_2CF_3 \xrightarrow{RS^-} (CF_3)_2C^--CF(SR)CF_2CF_3 \xrightarrow{-F^-} (CF_3)_2C=C(SR)CF_2CF_3 \quad (1)$$

$$\xrightarrow{RS^-} (CF_3)_2C(SR)-C^-(SR)CF_2CF_3 \xrightarrow{-F^-} (CF_3)_2C(SR)-C(SR)=CFCF_3$$

$$\xrightarrow[\text{1,4-elimn}]{-RSF} (CF_3)_2C=C(SR)CF=CF_2$$

$$RSF + RS^- \longrightarrow RSSR + F^- \qquad\qquad (2)$$
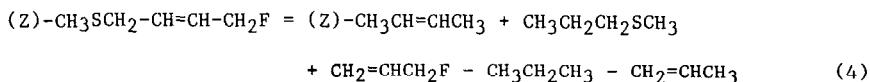
However, there appear to be several problems associated with this mechanism. The first, as noted by Ishikawa and Maruta themselves, it is rare for a neutral species containing a $-CF_3$ group to eliminate any fluorine containing species whether it be a sulfenyl fluoride or HF. Examples of facile fluorine loss have been chronicled for the recently prepared [2] trifluoromethyl alcohol and amine. However, it appears probable that elimination of HF is faciliated by deprotonation to form CF_3O^- and CF_3NH^- as we note that trifluoromethyl methane, CF_3CH_3, has high thermal stability. To demonstrate that this difference is a kinetic as opposed to thermodynamic phenomenon, consider the related monofluoro analogs, CH_2FNH_2, CH_2FOH and CH_2FCH_3 for which only the last is isolable at room temperature even though ab-initio calculations [3] show HF loss to comparably endothermic in all three cases: 86, 123 and 76 kJ mol^{-1} respectively (4.184 kJ = 1 kcal).

In that monofluoro derivatives mimic the trifluoro compounds of greatest relevance to this paper, they will be used as mimics in what follows. In particular, this assumption will be used in the estimation of the energetics of the 1,4-elimination reaction suggested by Ishikawa and Maruta. Furthermore, admitting the large and often unexpected changes in molecular energetics resulting from extensive fluorination of a molecule, nonetheless this step will be mimicked by the following far simpler reaction:

$$(Z)-CH_3SCH_2-CH=CH-CH_2F \longrightarrow CH_3SF + CH_2=CH-CH=CH_2. \qquad (3)$$
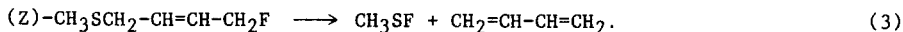
There is no experimental thermochemical data on the above fluorothioether, nor on CH_3SF nor on any other sulfenyl fluoride. It is thus necessary to estimate the heat of formation of both species of interest. 'Macro-incrementation reactions' [4], a recently chronicled approach that uses

'whole molecules' instead of group increments,* will be used to predict the desired data. In particular, for (Z)-CH₃SCH₂-CH=CH-CH₂F, macro-incrementation reaction (4) will be used:

$$(Z)-CH_3SCH_2-CH{=}CH-CH_2F = (Z)-CH_3CH{=}CHCH_3 + CH_3CH_2CH_2SCH_3$$

$$+ CH_2{=}CHCH_2F - CH_3CH_2CH_3 - CH_2{=}CHCH_3 \qquad (4)$$

Using literature values [5] for the heats of formation of all the above species on the right, the predicted heat of formation of the fluoro-thioether is -139 kJ mol⁻¹. (Most precisely, this value is for the gaseous species, a phase that was chosen to allow for the greatest ease of comparison of theory and experiment and one expected to be generally valid for descriptions of nonpolar species and their reactions.) The desired value for CH₃SF may be derived using macroincrementation reaction (5) wherein the particular effects of gem di-fluoro substitution [6] have been explicitly included:

$$CH_3SF = 1/2[(CH_3)_2S + SF_2] + \{HSF - 1/2(H_2S + SF_2)\} \qquad (5)$$
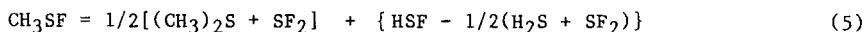
Using the data for SF₂ from reference [7] and the ab-initio energies from reference [8] to derive the value for the term in the { }, $\Delta H_f^{\circ}(g, CH_3SF)$ is found to be -142 kJ mol⁻¹. Admitting for all of the above uncertainties and assumptions in the estimates, combining the requisite numbers results in elimination reaction (3) being endothermic by 106 kJ mol⁻¹. In addition, reaction (3) as written has a marked entropy of activation as have the numerous other reactions with cyclic transition states [9]. (Reaction (3) and the earlier elimination reaction of Ishikawa and Maruta is even more unlikely were the (E)-fluorothioether chosen to be the

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*This "approach assumes that if for each of two sets of molecules the total number of bonds, atom and structural types is the same, then the total heat of formation of each set is the same. Then, if all but one of the heats are available the remaining one can be estimated by simple arithmetic. It deals with ... interactions much more explicitly but less universally by embedding these corrections in the heat of formation of the individual molecules which among them possess the desired bonding charac-teristics ... [and so] maximizes the direct use of available ... data."
(H.M. Rosenstock, et. al., op. cit., p. 26.)

reaction intermediate.) It would appear that the literature mechanism is unlikely as it is doubtful that the 'real-life' substituents can modify the energetics sufficiently to reverse the above conclusion. And yet the seemingly anomalous products are formed in good yield.

ALTERNATIVE MECHANISM

The proposed mechanism accepts that of the literature as far as formation of the fluoro-dithioether $(CF_3)_2C(SR)-C(SR)=CFCF_3$ is concerned. However, consider nucleophilic attack of the thiolate on the SR attached to the tertiary carbon:

$$RS^- + (CF_3)_2C(-SR)-C(SR)=CF-CF_3 \longrightarrow [(CF_3)_2C...C(SR)...CF-CF_3]^- + RSSR \quad (6)$$
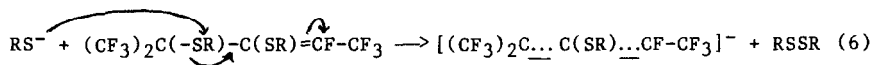
Such reactions are precedented [10] and in addition, this reaction is facilitated because the leaving group, a trifluomethylated allyl anion is highly stabilized. Loss of F^- from this anion results in the most stable diene, $(CF_3)_2C=C(SR)-CF=CF_2$, the observed product.

It will be noted that the current mechanism simultaneously lessens the entropy constraints implicit in the literature cyclic transition state and bypasses the formation of the sulfenyl fluoride. Ishikawa and Maruta report no product that is unequivocally due to this intermediate such as the trifluorosulfurane, RSF_3 [11]. Should the reader insist that the intermediacy of a sulfenyl fluoride is required in order to explain some of the minor byproducts of the reaction, it is to be noted that nucleophilic displacement on fluorine [12] in $(CF_3)_2C=C(SR)CFFCF_3$ yields the above mentioned stabilized allyl anion and the desired RSF species. In summary, it is seen that all of the literature products may be explained by postulating well-precedented nucleophilic displacement reactions rather than an intriguing, and seemingly still unprecedented, elimination reaction of sulfenyl fluorides from trifluoromethyl thioethers. Finally, noting that only 'normal' products of F-propene dimers were formed [13] in the reaction with N- and O-nucleophiles is compatible with the general absence of nucleophilic displacement reactions on nitrogen and oxygen by nitrogen and oxygen bases.

CONCLUSION

In conclusion, it is found that an alternative, well-precedented mechanism can account for the seemingly anomalous reaction of F-propene dimers with thiolate ions.

ACKNOWLEDGEMENTS

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