Stabilizing Interactions between Substituents Attached to the Same Saturated Carbon Atom. Enthalpies of Addition of Methanol, Pyrrolidine, and 1-Butanethiol to 1,1-Dichloro-2,2-difluoroethylene[1]

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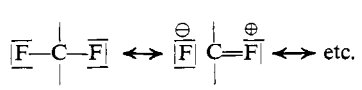
Abstract: Enthalpies of addition of methanol, pyrrolidine, and 1-butanethiol to 1,1-dichloro-2,2-difluoroethylene to give 1,1-difluoro-2,2-dichloroethyl derivatives have been measured in solution. From determinations and estimates of enthalpies of solution and of vaporization, it is calculated that the gas phase additions are exothermic by 37.2, 36.3, and 30.0 kcal/mol, respectively. From these and literature data it is estimated that the additions of methanol, pyrrolidine, butanethiol, hydrogen bromide, and chlorine to 1,1-dichloro-2,2-difluoroethylene are more exothermic than their additions to ethylene by 21.1, 18.9, 8.2, 4.3, and −2.7 kcal/mol, respectively. These results show that compounds with fluorine atoms attached to the same saturated carbon atom as oxygen, nitrogen, and, to a lesser extent, sulfur atoms are stabilized relative to the corresponding hydrogen compounds. The significance of these observations is discussed.

The disproportionation of methyl fluoride to methane and carbon tetrafluoride is exothermic by about 36 kcal/mol of carbon tetrafluoride. Stabilization of a one-carbon compound by an amount equal to the resonance energy of benzene (the disproportionation of cyclohexene to cyclohexane and benzene is exothermic by 36 kcal/mol of benzene) shows that stabilizing interactions of groups attached to the same saturated carbon atom are large enough to merit further investigation. Suggestions that the tendency of fluorine atoms to cluster around the same saturated carbon atom is due to stabilization by double-bond–no-bond (db–nb) resonance[2,3]



$$|\overline{\underline{\text{F}}}-\underset{|}{\overset{|}{\text{C}}}-\overline{\underline{\text{F}}}| \longleftrightarrow |\overset{\ominus}{\overline{\underline{\text{F}}}}|\ \underset{|}{\overset{|}{\text{C}}}=\overset{\oplus}{\overline{\text{F}}}| \longleftrightarrow \text{etc.}$$

were reviewed recently[4] and it was pointed out that attachment of two oxygen atoms to the same saturated carbon atom leads to an increase in thermodynamic stability that is about as large as that associated with the clustering of two fluorine atoms around a saturated carbon atom. In order to learn whether this "clustering effect" is best considered in terms of db–nb resonance or of some other explanation, it seemed desirable to study cases of mixed interactions between two different atoms attached to the same saturated carbon atom. Cases in which fluorine, the most electronegative of the elements, was attached to the same saturated carbon atom as alkoxy and amino groups, which have strong resonance electron-donating ability, were of particular interest. Compounds containing these structural features appear, from molecular structure evidence, to be stabilized, relative to the analogous compounds containing hydrogen instead of fluorine. For example, the carbon–nitrogen bond in tris(trifluoromethyl)amine (length, 1.43 ± 0.03 Å)[5] appears to be shorter than the typical bond between sp^3 carbon and tricovalent nitrogen (1.472 ± 0.005 Å),[6] and the carbon–oxygen bond in bis(trifluoromethyl) ether (1.36 ± 0.04 Å)[7] appears to be shorter than the typical bond between sp^3 carbon and oxygen (1.426 ± 0.005 Å).[6] In contrast, the bonds from the central atom to the trifluoromethyl groups in bis(trifluoromethyl) sulfide (C–S bond length 1.828 ± 0.015)[7] and tris(trifluoromethyl)phosphine (C–P bond length 1.94 ± 0.02 Å)[6] are longer, if anything, than typical bonds between sp^3 carbon and divalent sulfur (1.817 ± 0.015 Å)[6] and between sp^3 carbon and trivalent phosphorus (1.841 ± 0.005 Å),[6] respectively. However, the differences in bond lengths brought about by replacing hydrogen by fluorine in these cases are on the order of the experimental uncertainty. Furthermore, the exact relationship between bond lengths and thermodynamic stabilities is unknown. Therefore, we have obtained thermochemical data on the extent of interaction of fluorine atoms with other atoms and groups attached to the same saturated carbon atom by measuring the enthalpies of addition of various compounds to 1,1-dichloro-2,2-difluoroethylene.

Results

A Bunsen ice calorimeter was used to determine the enthalpies of addition of methanol, 1-butanethiol, and pyrrolidine to 1,1-dichloro-2,2-difluoroethylene at 0°. Attempts to add hydrogen fluoride to this olefin at room temperature and below were unsuccessful, even though both alcohol and dipolar aprotic solvents were used, and the reaction was attempted with and without fluoride

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(1) Part XIII in the series "Polar Effects on Rates and Equilibria." For the preceding part see J. Hine, L. G. Mahone, and C. L. Liotta, *J. Am. Chem. Soc.*, **89**, 5911 (1967). This work was supported in part by grant GP-4445 from the National Science Foundation. Preliminary presentation: F. E. Rogers and J. Hine, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. S168.

(2) *Cf.* L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 314–315.

(4) J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963).

(5) R. L. Livingston and G. Vaughan, *ibid.*, **78**, 4866 (1956).

(6) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959," Special Publication No. 18, The Chemical Society, London, 1965, pp S19s–S23s.

(7) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p M120.

ions (sometimes from the organic-soluble tetrapropylammonium fluoride) as catalysts.

To obtain the enthalpies of reaction of the pure liquid reactants to give the pure liquid products, and to obtain the enthalpies of reaction in the gas phase, enthalpies of solution and of vaporization are needed. The following thermochemical scheme is used.

$$\begin{tikzcd}
CF_2{=}CCl_2(soln) & + & HX(soln) \arrow[r, "\Delta H^\circ_r(soln)"] & XCF_2CHCl_2(soln) \\
CF_2{=}CCl_2(l) \arrow[u, "\Delta H^\circ_1"'] \arrow[d, "\Delta H^\circ_4"] & & HX(l) \arrow[u, "\Delta H^\circ_2"'] \arrow[d, "\Delta H^\circ_5"] & XCF_2CHCl_2(l) \arrow[u, "\Delta H^\circ_3"'] \arrow[d, "\Delta H^\circ_6"] \\
CF_2{=}CCl_2(g) & + & HX(g) \arrow[r, "\Delta H^\circ_r(g)"] & XCF_2CHCl_2(g)
\end{tikzcd}$$

In the reactions of methanol and butanethiol

$$\Delta H^\circ_{\text{exptl}} = \Delta H^\circ_r(\text{soln}) + \Delta H^\circ_1$$

$$\Delta H^\circ_r(\text{g}) = \Delta H^\circ_{\text{exptl}} + \Delta H^\circ_2 - \Delta H^\circ_3 - \Delta H^\circ_4 - \Delta H^\circ_{56} + \Delta H^\circ$$

In the reaction of pyrrolidine

$$\Delta H^\circ_{\text{exptl}} = \Delta H^\circ_r(\text{soln}) + \Delta H^\circ_2$$

$$\Delta H^\circ_r(\text{g}) = \Delta H^\circ_{\text{exptl}} + \Delta H^\circ_1 - \Delta H^\circ_3 - \Delta H^\circ_4 - \Delta H^\circ_5 + \Delta H^\circ_6$$

The values of the various ΔH's determined at 0° are listed in Table I, as are the values of ΔH°_r(g) calculated from them. The enthalpy of solution of 1-(2,2-dichloro-1,1-difluoroethyl)pyrrolidine was not determined because we were not able to prepare the material in a sufficiently pure form, free from significant amounts of acidic impurities. Therefore the enthalpy of solution of this compound was assumed to be the same as that of pyrrolidine. The other enthalpies of solution are average values, determined at concentrations around those present in the determinations of enthalpies of addition. The enthalpies of vaporization at 0°, ΔH°_4, ΔH°_5, and ΔH°_6, were estimated from the boiling points of the compounds, using the method of Klages,[8] in all cases except those of methanol[9] and 1-butanethiol[10] where the values at 25° and the method of Klages for estimating the change in enthalpy of vaporization with changing temperature were used.

Table I. Enthalpies at 0° [a]

	HX		
	MeOH[b]	BuSH[c]	Pyrrolidine[d]
$\Delta H^\circ_{\text{exptl}}$	-31.2 ± 0.7	-28.8 ± 0.3	-33.8 ± 0.4
ΔH°_2	0.0	0.35 ± 0.03	
ΔH°_3	-0.57 ± 0.09	-0.79 ± 0.13	
ΔH°_4	6.42	6.42	6.42
ΔH°_5	9.40	9.12	8.90
ΔH°_6	9.25	13.19	12.79
ΔH°_r(g)	-37.2	-30.0	-36.3[e]

[a] In kilocalories/mole. [b] "soln" refers to methanol solution. [c] "soln" refers to N,N-dimethylformamide solution. [d] "soln" refers to ether solution. [e] Assuming that ΔH°_1 and ΔH°_3 are equal.

We estimate the uncertainty of ΔH°_r(g) for the reactions of methanol and 1-butanethiol to be on the order of 2 kcal/mol. For pyrrolidine, where the reaction product is less stable and where the product analysis was less satisfactory, the result may be in error by several kilocalories/mole.

Discussion

The only other additions to 1,1-dichloro-2,2-difluoroethylene for which we have found enthalpy measurements recorded are those of hydrogen bromide[11] and chlorine,[12] which were found to be exothermic by 23.0 and 41.1 kcal/mol, at 94 and 90°, respectively, in the gas phase. In order to learn more about the extent to which the differences in enthalpies of addition of the various compounds to difluorodichloroethylene are due to interactions involving the fluorine atoms, these enthalpies should be compared with the enthalpies of addition to 1,1-dichloroethylene. Unfortunately, neither the enthalpies of addition to 1,1-dichloroethylene nor the data from which they may be calculated appear to be available, and they cannot be determined with the equipment at hand. We have chosen ethylene as the reference olefin. This is equivalent to defining hydrogen as the reference substituent, interactions with which are defined as zero. Enthalpies of addition to ethylene were calculated from the enthalpies of formation of ethylene,[13] the reactants, methanol,[9] butanethiol,[10] and hydrogen bromide,[14] and the products, ethyl methyl ether,[15] butyl ethyl sulfide,[10] and ethyl bromide,[16] giving the values −16.1, −21.8, and −18.6 kcal/mol, respectively (all in the gas phase at 25°). The enthalpy of addition of chlorine to ethylene at 82° has been found to be −43.7 kcal/mol by direct measurement.[17] The enthalpy of addition of pyrrolidine to ethylene to give 1-ethylpyrrolidine was estimated to be −17.4 kcal/mol by use of the group contributions of Benson and Buss.[18, 19]

Comparison of an enthalpy of addition to dichlorodifluoroethylene with an enthalpy of addition to ethylene is equivalent to subtracting one thermochemical equation from another. For the five adding reagents under consideration such subtraction, after correction to 25°, gave the following equations.[21]

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(8) F. Klages, *Chem. Ber.*, **82**, 358 (1949).

(9) J. H. S. Green, *Quart. Rev.* (London), **15**, 125 (1961).

(10) H. Mackle and P. A. G. O'Hare, *Tetrahedron*, **19**, 961 (1963).

(11) J. R. Lacher, K. R. Lea, C. H. Walden, G. G. Olson, and J. D. Park, *J. Am. Chem. Soc.*, **72**, 3231 (1950).

(12) J. R. Lacher, J. J. McKinley, C. Walden, K. Lea, and J. D. Park, *ibid.*, **71**, 1334 (1949).

(13) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Brown, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(14) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950.

(15) G. Pilcher, A. S. Pell, and D. J. Coleman, *Trans. Faraday Soc.*, **60**, 499 (1964).

(16) P. Fowell, J. R. Lacher, and J. D. Park, *ibid.*, **61**, 1324 (1965).

(17) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Am. Chem. Soc.*, **60**, 2764 (1938).

(18) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

(19) The enthalpy of addition was assumed to be equal to $[N\text{–(C)}_3] + 3[C\text{–(N)(H)}_3] + [C\text{–(H)}_3\text{(C)}] + [C\text{–(C)(N)(H)}_2] - [C\text{–(N)(H)}_3] - [N\text{–(C)}_2\text{(H)}] - 2[C\text{–(N)(H)}_3] - \Delta H_f(C_2H_4)$. This would give the enthalpy of addition of any secondary amine to ethylene. From the simpler method of bond contributions a value of −17.0 kcal/mol is obtained. The simpler (and older) methods of Klages and Franklin, as modified by Wheland,[20] give values of −15.4 and −20.4 kcal/mol, respectively.

(20) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, Chapter 3.

(21) Corrections to 25° were made by use of known heat capacities or heat capacities estimated from the bond contributions of Benson and Buss.[18] None of the corrections was larger than 0.1 kcal/mol.

	ΔH°_{298}(g), kcal/mol
$MeOCH_2CH_3 + CF_2{=}CCl_2 \longrightarrow MeOCF_2CHCl_2 + CH_2{=}CH_2$	−21.1
$C_4H_8NCH_2CH_3 + CF_2{=}CCl_2 \longrightarrow C_4H_8NCF_2CHCl_2 + CH_2{=}CH_2$	−18.9
$BuSCH_2CH_3 + CF_2{=}CCl_2 \longrightarrow BuSCF_2CHCl_2 + CH_2{=}CH_2$	−8.2
$BrCH_2CH_3 + CF_2{=}CCl_2 \longrightarrow BrCF_2CHCl_2 + CH_2{=}CH_2$	−4.3
$ClCH_2CH_2Cl + CF_2{=}CCl_2 \longrightarrow ClCF_2CCl_3 + CH_2{=}CH_2$	2.7

The differences in the first four values are due to α interactions with fluorine plus β interactions with chlorine; the last value also contains the effect of α-chloro and β-fluoro interactions. It seems clear that at least some of these interactions are unusually large. According to the first-order approximation (the rule of additivity of bond properties) of Benson and Buss,[18] which is usually correct within 5 kcal/mol, all these reactions should be thermoneutral; yet their enthalpies vary over a range of more than 23 kcal/mol. Examples of large nonbonded interactions due to destabilizing steric effects are known but seem highly unlikely in the present case. A common type of nonbonded interaction is that correlatable by the Hammett and Taft equations. In such cases destabilization results when substituents with the same type of polar effect are transferred from different molecules to the same molecule or when such substituents are moved closer together in the same molecule.[22] The extent of this destabilization is proportional to the product of the substituent constants of the substituents in question and a proportionality constant (τ) that increases as the substituents are moved closer together. Therefore, β interactions with chlorine should tend to cause the transfer of the methoxy, pyrrolidinyl, butylthio, and bromo substituents from the ethyl group to the 1,1-difluoro-2,2-dichloroethyl group to be endothermic. None of the β interactions should be any larger than the interaction between two chlorine atoms attached to adjacent carbon atoms. This interaction may be estimated from the heats of formation of ethyl chloride,[23] ethylene dichloride,[24] and ethane[13] to be 1.1 kcal/mol, or from the heats of formation of *n*-propyl chloride,[23] isopropyl chloride,[23] 1,2-dichloropropane,[24] and propane[13] to be 0.6 kcal/mol. Although these measures of the magnitude of the β-dichloro interaction may contain a kilocalorie or so of experimental error, it seems unlikely that β interactions should contribute more than about 4 kcal/mol to the enthalpies of reaction of the four C_2H_5X's with dichlorodifluoroethylene. The contribution to the *differences* in enthalpies of reaction should be even smaller. We therefore attribute most of the differences in enthalpies of reaction to α interactions with fluorine.

It therefore appears that the stabilizing α interaction between methoxy and fluorine is a large one and the one between pyrrolidinyl and fluorine is probably somewhat smaller or in any case not significantly larger. If the α interactions we are studying are due to db–nb resonance, the no bonding would be done largely by the highly electronegative fluorine atoms; therefore the amount of stabilization (after correction for destabilization by Hammett–Taft-type effects) should increase with increasing ability of the interacting substituent to use its unshared electron pairs for double bonding (+T effect).[22] Inasmuch as we started this investigation without a critical analysis of the usually accepted order of the +T effect of various substituents ($R_2N >$ RO > F > Cl > Br and RO > RS > Cl), we were not surprised that the α interactions of fluorine with bromine and butylthio were much less stabilizing than those with methoxy and pyrrolidinyl. However, the fact that the pyrrolidinyl interaction was no larger than the methoxy interaction seemed at first to provide strong evidence against the concept of db–nb resonance. The usually accepted idea that the magnitude of the +T effect decreases on going to the right in the periodic table finds quantitative support in the differences between $\sigma_p{}^+$ and σ_p for various substituents; $\sigma_p - \sigma_p{}^+$ is 0.87, 0.51, and 0.14 for dimethylamino, methoxy, and fluoro substituents, and it is 0.60 and 0.11 for methylthio and chloro, respectively.[22] However, the fact that the substituents we are considering are better electron donors in the *para* than in the *meta* position has also been attributed largely to the +T effect. When the +T effect is measured in terms of the difference between σ_m and σ_p, using σ^n values where available so as to consider only the resonance interaction with the benzene ring, the values 0.17, 0.29, and 0.28 are obtained for dimethylamino, methoxy, and fluoro substituents, respectively. Thus, according to $\sigma_p - \sigma_p{}^+$ values the +T effect of dimethylamino is larger than that of methoxy, whereas according to $\sigma_m{}^n - \sigma_p{}^n$ values it is not. Consequently, it is not clear whether the concept of db–nb resonance would necessarily lead to the prediction that the α interaction of fluorine with an amino group would be larger than the analogous interaction with an alkoxy group.

Additional relevant data may be found in recent reports concerning the effect of β-fluorine substituents on rates of carbanion formation.[25-28] Interpretation of data on rates of exchange at the bridgehead of fluorinated bicyclic ring systems[26,27] is complicated by the effect of the amount of s character of the C–H bond on the acidity of the bridgehead hydrogen[29] and by the fact that steric hindrance is relatively small. The conclusion to be drawn from the present data on 9-substituted fluorenes[28] depends in part on whether data on the unsubstituted compound are included in the linear free energy correlation. In spite of these shortcomings these reports provide evidence that β-fluoro substituents exert most of their influence on carbanion formation by inductive and/or field effects and relatively little (if any) by resonance.

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(22) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 4.

(23) J. Davies, J. R. Lacher, and J. D. Park, *Trans. Faraday Soc.*, **61**, 2413 (1965).

(24) J. R. Lacher, A. Amador, and J. D. Park, *ibid.*, **63**, 1608 (1967).

(25) S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964).

(26) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, **21**, 2997 (1965).

(27) A. Streitwieser, Jr., and D. Holtz, *J. Am. Chem. Soc.*, **89**, 692 (1967).

(28) A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967).

(29) *Cf.* J. Meinwald, C. Swithenbank, and A. Lewis, *ibid.*, **85**, 1880 (1963).

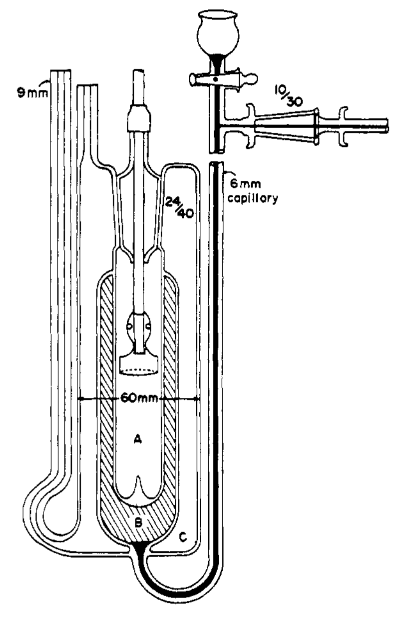
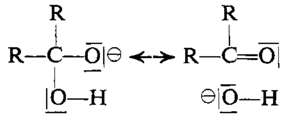


Figure 1. Calorimeter.

Another case in which the attachment of a substituent capable of strong resonance electron donation to the same saturated carbon as a relatively electronegative atom does not result in any marked resonance effect may be found when the acidity of *gem*-diols is considered. It might be expected that stabilization of the conjugate base of such a diol by db–nb resonance



$$\mathrm{R{-}\overset{R}{\underset{|\overline{O}{-}H}{C}}{-}\overline{O}|^{\ominus} \longleftrightarrow R{-}\overset{R}{\underset{^{\ominus}|\overline{O}{-}H}{C}}{=}\overline{O}|}$$

would be greater than the analogous stabilization of the diol. However, Bell[30] has reported that the Taft equation correlations of the acidity of alcohols and *gem*-diols may be combined if σ^* for the hydroxy substituent is taken as 1.28. Since this value is smaller than that (1.568) obtained by multiplying[22] σ^* for the hydroxymethyl substituent by 2.8 or that (1.34) obtained from a correlation of the basicity of amines,[31] no increase in acidity of the type to be expected from db–nb resonance occurs.

The concept of db–nb resonance would become less useful if a suitable alternative rationalization could be devised for the particularly large deviations from additivities of bond properties that are observed in compounds with several fluorine, oxygen, and/or nitrogen atoms attached to the same saturated carbon atom. Pearson and Songstad have discussed the tendency of fluorine and oxygen atoms to cluster around a saturated carbon atom in terms of the principle of hard and soft acids and bases.[32] However, it is not clear what the relative hardnesses of NR_2^-, OR^-, and F^- are, and therefore it is not clear what the principle of hard and soft acids and bases would predict in the present case.

Experimental Section[33]

Reagents. The 1,1-dichloro-2,2-difluoroethylene (Peninsular Chemresearch, Inc.) available contained about 5% impurities (apparently largely 1,2-dichloro-1,2-difluoroethylenes). Preparative glpc, using a fluorosilicone QF-1 column at 0°, reduced the concentration of impurities to about 0.2%. Methanol was dried by distillation from magnesium.

Methyl 1,1-difluoro-2,2-dichloroethyl ether was prepared by the base-catalyzed addition of methanol to dichlorodifluoroethylene.[34] The methanolic reaction solution was poured into water and the ether extracted with methylene chloride. The extract was dried over Drierite and distilled. Two of the fractions collected between 97 and 98° at atmospheric pressure were found by glpc analysis using a diethylene glycol succinate column to contain a total of 0.06% of methylene chloride and methanol as the only impurities.

Fractional distillation of 1-butanethiol yielded material that was 99.8% pure, according to glpc analysis using a Carbowax 20M column.

The N,N-dimethylformamide used (said to contain 0.1% water and 0.01% dimethylamine) was dried over Linde Molecular Sieve Type 4A, and distilled at 55° (90 mm).

The triethylamine used was found by glpc analysis to be 99.9% pure.

Fractional distillation of pyrrolidine yielded material that was 99.6% pure, according to glpc analysis.

Anhydrous reagent ether was dried over Linde Molecular Sieve, Type 4A.

Calorimetric Measurements. The Bunsen ice calorimeter used, whose design is shown in Figure 1, resembles one described by Speakman and Stott[35] except that an outer jacket (C) has been added. Chamber B was filled with degassed distilled water and mercury. At the start of a run, the calorimeter was cooled to 0°; the capillary side arm was not attached but the 10/30 joint was plugged and the stopcock opened. Chamber C was filled with water and A about two-thirds filled with acetone, both at 0°. A test tube containing solid carbon dioxide was lowered into chamber A and swirled. At first the water in B became supercooled, but rather suddenly a large amount of ice formed. Most of this ice was allowed to melt; when only a small amount of ice on the outer surface of chamber A remained, the tube of solid carbon dioxide was again introduced into A, and a mantle of ice of uniform thickness was thus built up in B on the outer surface of A. After as much of the acetone as possible had been aspirated from A, dry nitrogen was passed through A to complete the removal of acetone. Chamber A was washed with several portions of the solution to be added at 0° and then the appropriate amount of the solution was added. A weighed amount of the limiting reactant was sealed into a fragile spherical glass ampoule of such a size that the ampoule was mostly filled. This ampoule was attached to the bottom of the stirring rod by use of a drop of hot polyethylene in such a fashion that the tip resulting from sealing was oriented about 45° downward.[36] The calorimeter was then placed in a 1-gal dewar flask and covered with cracked ice to a level somewhat above the top of the 24/40 joint. The dewar flask was wrapped in 1-in. foam rubber and fitted with a foam rubber lid through which the stirrer and capillary tube protruded. The exposed parts were covered with a plastic bag and the entire apparatus allowed to stand for several hours. The constant-bore capillary side arm[37] (Ace Glass Catalog No. 8700) was attached through the 10/30 joint and the length of the mercury thread in it adjusted by use of the stopcock.[38] The

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[30] R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).

[31] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

[32] R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

[33] Except where otherwise indicated all pmr spectra were determined on Varian A-60 spectrometers using tetramethylsilane as an internal standard. Infrared spectra were determined on a Perkin-Elmer Model 337 grating spectrophotometer.

[34] *Cf.* W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

[35] J. B. Speakman and E. Stott, *Trans. Faraday Soc.*, **34**, 1204 (1938).

[36] If the tip was oriented directly downward it sometimes interfered with the breaking process. If it was oriented upward part of the reactant was sometimes trapped behind a small air bubble. In later runs somewhat larger ampoules were used so that enough air was contained for them to float. In these cases it was not necessary to seal them to the stirrer.

[37] The constancy of bore of this capillary had been tested by observing the length (to 0.1 mm) of a mercury thread about 2 cm long in nine different locations in the tube. No reading deviated from the mean by as much as 0.2 mm and the average deviation was 0.06 mm.

[38] This was a standard glass stopcock in our work but subsequently Dr. George Kriz observed that difficulties, such as separation of the

mercury thread was then observed to drift steadily outward, as an increasing amount of the pure water in B was frozen by the saturated air–water–ice system in the dewar flask. To insulate chambers A and B from the surrounding medium and thus to decrease the rate of drift of the mercury thread, chamber C was drained of water, flushed several times with carbon dioxide gas, and then allowed to remain full of carbon dioxide. In order to observe the prevailing rate of heat leakage the length of the mercury thread in the capillary side arm was recorded at intervals. After the drift rate had been steady for at least 20 min, the ampoule was smashed against the glass spike at the bottom of chamber A and the reaction solution stirred by eight vertical strokes of the stirrer. The solution was stirred again in as nearly the same way as possible by repeating the sequence of eight strokes from five to eight times at intervals of 1 or 2 min. Experiments using aqueous acid and base and an indicator showed that mixing of the solution was complete at the end of the second stirring sequence. Other test experiments showed that the breaking of the ampoule and the stirring procedure did not have any clearly detectable heat effect. The length of the mercury thread was recorded at the end of each stirring sequence and after the stirring was stopped at intervals that increased in length as the rate of movement of the thread decreased. After a constant rate of drift of the thread had again been established (at least 40 min after breaking the ampoule) observations were discontinued, and the reaction mixture was analyzed. The change in the length of the mercury thread attributable to the reaction was determined by the method of Dickinson.[39] From this result the change in volume was calculated; then, from the difference in densities of water and ice,[40] the amount of ice that had melted (or formed) was calculated; finally, from the heat of fusion of ice,[41] the amount of heat evolved (or absorbed) was calculated. The drift rates usually corresponded to a rate of loss of heat from the system of 3 ± 1 cal/hr. The amounts of heat given off in the addition reactions studied were on the order of 120 cal. The changes in the length of the mercury thread were on the order of 160 mm. The amounts of heat given off in the enthalpy of solution measurements were no more than 11 cal. Although a smaller capillary was used in these experiments the change in the length of the mercury thread was no more than about 100 mm.

Five determinations of the enthalpy of neutralization of about 2.5 ml of 2.509 *M* hydrochloric acid by 30 ml of 0.2510 *M* sodium hydroxide solution gave values of 14.91, 15.34, 15.24, 14.81, and 14.80 kcal/mol. The average value, 15.02 ± 0.22 kcal/mol, is 3% smaller than the value that should have been obtained as calculated from the calorimetrically determined heat of dissociation of water at 0° and infinite dilution[42] and the heats of dilution[43] of sodium hydroxide, hydrochloric acid, and sodium chloride.

Enthalpy of Addition of Methanol to 1,1-Dichloro-2,2-difluoroethylene. In these runs the ampoule contained about 0.5 g of 1,1-dichloro-2,2-difluoroethylene and the calorimeter contained 30 ml of about 0.1 *M* sodium methoxide in methanol. Half the total change in the length of the mercury thread had occurred in about 5 min. This value for the half-time of the reaction in the presence of 0.1 *M* sodium methoxide is in good agreement with the value *ca.* 4 min that may be calculated from the published rate constant,[45] especially when it is considered that even in the neutralization of hydrochloric acid by sodium hydroxide, which is essentially instantaneous, the half-time for the change in mercury thread length is somewhat more than 1 min. The mercury thread length was followed for at least 90 min after breaking the ampoule, *i.e.*, for at least an hour past 99.5% reaction. A 10-ml sample of the reaction mixture was then titrated to the phenolphthalein end point with standard hydrochloric acid. In comparing the strength of the sodium methoxide before and after the reaction, it was assumed that the 1,1-dichloro-2,2-difluoroethylene had diluted the methanol solution by an amount equal to its volume, which was calculated from its weight by assuming that its density was equal to that of the isomeric 1,2-dichloro-1,2-difluoroethylenes.[46] The calculated extents of dilution were between 1.0 and 1.1%. The average number of moles of base used up was equal to 0.7% of the number of moles of dichlorodifluoroethylene used.

A microsyringe with a Chaney adapter (whose setting was not changed during the course of the research) was used to inject several 3.00-μl samples of the reaction solution into a glpc apparatus containing a diethylene glycol succinate column at 60°. A weighed amount (about 0.14 g) of methyl 1,1-difluoro-2,2-dichloroethyl ether was added to a 10-ml aliquot of the reaction solution and 3.00-μl samples of the resulting solution were subjected to glpc analysis under the same conditions used for the original reaction solution. From the relative areas under the ether peaks (determined using a planimeter) the concentration of ether in the reaction solution was calculated. The yields were found to be 101.4 ± 2.0%. No by-products were found by glpc analysis.

Enthalpy of Addition of 1-Butanethiol to 1,1-Dichloro-2,2-difluoroethylene. In these studies an ampoule containing about 0.58 g (4.4 mmol) of 1,1-dichloro-2,2-difluoroethylene was broken under a solution of 0.060 ml (0.3 mmol) of triethylamine and 2.80 ml (26 mmol) of 1-butanethiol in 30 ml of N,N-dimethylformamide. Inasmuch as half of the change in the length of the mercury thread had occurred in about 3 min, the half-time of the reaction must be less than 3 min. Hence the reaction, which was followed for more than an hour, must have been more than 99.5% complete in about 20 min. The reaction solution was analyzed by glpc of 3-μl samples on a Carbowax 20M column. The planimetrically determined areas were compared with those obtained using standard solutions of butyl 1,1-difluoro-2,2-dichloroethyl sulfide of about the same concentration. The average precision obtained with the standard solutions was 2.6%. The average yield in the calorimetric experiments was found to be 102% with an average deviation of 2%.

The enthalpy of solution of butanethiol in dimethylformamide was determined in the presence of the same concentration of triethylamine that was used in the enthalpy of addition measurements. The enthalpy of solution of butyl 1,1-difluoro-2,2-dichloroethyl sulfide was determined in the presence of the same concentration of butanethiol that was used in the enthalpy of addition measurements. No triethylamine was present because it was felt that the heat of reaction of the amine with small amounts of acidic impurities in the sulfide might give misleading results.

***n*-Butyl 1,1-Difluoro-2,2-dichloroethyl Sulfide.** The published method of preparing this compound[47] was modified in that we used triethylamine as the basic catalyst. Purification by preparative glpc appeared to result in the formation of additional impurity, inasmuch as material with several tenths of a per cent of an impurity with a significantly different retention time was found to continue to have about this amount of the impurity after several purification cycles. According to glpc analysis on a Carbowax 20M column, fractional distillation yielded 99.1% pure material, bp 82° (12.5 mm); satisfactory analysis for C, H, Cl, F, and S; ir (neat) 2975, 2940, 2880, 1450, 1165, 1060, 1040, 997, 827, and 750 cm^{-1}; pmr (at 100 MHz, neat) τ 4.2 (t, 1.0, J = 7 Hz, $\mathrm{C}H\mathrm{Cl_2}$), 7.1 (t, 2.0, J = 7 Hz, $\mathrm{S}CH_2$), *ca.* 8.4 (m, *ca.* 4.4, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), and 9.0 ppm (t, 3.1, J = 6 Hz, $\mathrm{C}H_3$). The 60 MHz pmr spectrum was similar to that obtained at 100 MHz except that the triplet at τ 9.0 appeared to be a doublet.

1-(2,2-Dichloro-1,1-difluoroethyl)pyrrolidine. Gradual addition of 3.7 g of pyrrolidine to 8 g of 1,1-dichloro-2,2-difluoroethylene in 30 ml of tetrahydrofuran at 0° gave a yellow solution that was distilled under vacuum after it had stood 1 hr. At 55–56° (5 mm) a colorless liquid was collected that became yellow and fumed on exposure to air. Upon storage at 0° the compound darkened in color while a solid separated and fumes were evolved.

Addition of *ca.* 0.7 ml of this liquid to *ca.* 1 ml of water resulted in a reaction that caused the water to boil. After an additional 2 ml of water had been added and the reaction mixture allowed to stand overnight, the organic layer was separated and distilled to give a colorless liquid, bp 90° (3 mm), that solidified (mp 36.5–39°).

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mercury thread (attributed to the presence of stopcock grease), could be decreased by use of a needle valve with a Teflon stem (Fischer and Porter Catalog No. 795-120).

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Recrystallization from ether–petroleum ether gave white needles: mp 45–46°; pmr ($CDCl_3$) τ 3.64 (s, 0.9), 6.4 (m, 4.0), and 8.1 ppm (m, 4.1); ir (CCl_4) in order of decreasing intensity 1660, 1690, 1420, 2990, 2890, 2960, and 1225 cm^{-1}. *Anal.* Calcd for $C_6H_9ONCl_2$: C, 39.59; H, 4.98; N, 7.69; Cl, 38.95. Found: C, 39.61; H, 5.04; N, 7.61; Cl, 38.75. The method of synthesis, analysis, and other properties provide strong evidence that this white solid is 1-(dichloroacetyl)pyrrolidine. However, in the only pertinent literature reference we have found,[48] this compound, formed by the reaction of pyrrolidine with ethyl dichloroacetate, was reported to be a liquid, $n^{25}D$ 1.5182. We therefore treated pyrrolidine with dichloroacetyl chloride, obtained a solid product with the same melting point and the same ir and pmr spectra as the one obtained using 1,1-dichloro-2,2-difluoroethylene, and assumed that our structural assignment was correct.

At the concentration and in the solvent used for calorimetric measurements the pmr spectrum of 1-(2,2-dichloro-1,1-difluoroethyl)pyrrolidine was too weak and too obscured by the solvent spectrum to be useful. The pmr spectrum of samples prepared in a number of different ways showed that 1-(dichloroacetyl)pyrrolidine was also present. However, when pyrrolidine and excess 1,1-dichloro-2,2-difluoroethylene were mixed in a carefully dried nmr tube at −80° and the spectrum measured at 0° within an hour, a triplet (J = 7 Hz) and two multiplets with relative areas of 1:4:4 were observed at τ 4.1, 6.85, and 8.1 ppm, respectively. The only other absorption clearly present was a small doublet (J = 7 Hz) of unknown origin at 8.7 ppm. In a similar experiment, 0.40 ml of 1,1-dichloro-2,2-difluoroethylene, 0.400 ml of chloroform, and 0.200 ml of pyrrolidine were mixed at −80° and then kept at 0° for 15 min. The only absorption besides that of the adduct was the chloroform singlet. From comparison of the area of the chloroform peak with the peaks at τ 4.1, 6.85, and 8.1 ppm, yields of 96 ± 7, 97 ± 8, and 104 ± 6% were calculated for the adduct.

Enthalpy of Addition of Pyrrolidine to 1,1-Dichloro-2,2-difluoroethylene. An ampoule containing about 0.26 g (3.6 mmol) of pyrrolidine was broken under solution of 3 ml (34 mmol) of 1,1-dichloro-2,2-difluoroethylene in 26 ml of diethyl ether. Inasmuch as half of the total change in length of the mercury thread had taken place in less than 2 min, the half-time of the reaction is probably less than 1 min. Hence the reaction, which was followed for at least 40 min, must have been more than 99.9% complete in 10 min or less. To try to insure that the solution was completely mixed as quickly as possible in this particularly rapid reaction, it was stirred about 30 times during the first 2 min of reaction.

Attempts to determine the stoichiometry of the reaction by quantitative hydrolysis to 1-(dichloroacetyl)pyrrole and hydrofluoric acid yielded no more than about 90% of the theoretical amount of acid. Analysis by glpc showed that the reaction mixture was decomposing during analysis to give a number of products.

Acknowledgment. We should like to acknowledge the help of Dr. Albert C. Ruggles who made the attempts at addition of hydrogen fluoride to dichlorodifluoroethylene.

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The Crystal Structure of a Friedel–Crafts Intermediate. Methyloxocarbonium Hexafluoroantimonate

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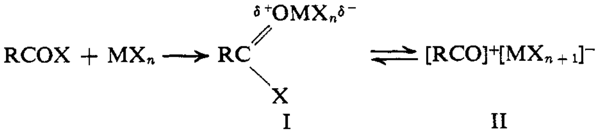
Abstract: Oxocarbonium ions are postulated intermediates in Friedel–Crafts acylations. Crystals of methyloxocarbonium hexafluoroantimonate, $[CH_3CO]^+[SbF_6]^-$, are monoclinic, space group $P2_1/m$, with unit cell dimensions a = 5.758, b = 7.783, c = 7.879 Å, and β = 101°3′, Z = 2. Three-dimensional X-ray data were collected by the precession method (Mo Kα radiation) and estimated visually. The structure was refined by full-matrix least squares to a reliability index R_1 = 5.6% for 799 observed reflections. The crystal structure provides direct proof of an ionic structure in the solid state, and confirms the hypothesis that the oxocarbonium ion is linear. Some structural evidence that the positive charge in the cation is largely localized on the central carbon is discussed, and a molecular orbital calculation supporting this hypothesis is described.

Oxocarbonium ions, $[RCO]^+$, are believed to be intermediates in Friedel–Crafts acylation reactions,[1] in which acyl halides react with aromatic derivatives to yield aromatic ketones. These reactions are catalyzed

$$RCOX + ArH \xrightarrow{MX_n} RCOAr + H^+ + X^-$$

by acidic halides, MX_n, which combine variously[1] with acyl halides to form donor–acceptor complexes (I), or to generate oxocarbonium ions (II). The crystal structures of two such donor–acceptor complexes, benzoyl chloride–aluminum chloride[2] and benzoyl chloride–antimony pentachloride,[3] have been reported. Since a 1:1 addition compound of boron trifluoride and acetyl fluoride was first identified as $[CH_3CO]^+[BF_4]^-$ by Seel,[4] the existence of a number of stable oxocarbonium salts (II) has been demonstrated by infrared studies of the solids and by nmr methods in solution.[5-10] The present



I

II

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