electrons will be more important than that with the carbon fraction, a^2. However, electron repulsion between electrons in different 5p orbitals is less than that between 5p and any core orbital. For example, in Hartree–Fock calculations on the iodine atom, the Coulomb repulsion integral $(5p_x5p_x/5p_z5p_z)$ = 0.69 rydberg whereas that for $(3d_i3d_i/5p_z5p_z)$ = 0.99 rydberg.[6]

The displacement of the point for hydrogen iodide from the alkyl iodide correlation line is plausibly explained by hyperconjugation. The iodine 5p levels are destabilized by interaction with appropriate σ orbitals on the alkyl group (hyperconjugation). This destabilization is partially offset by a stabilizing interaction with the corresponding σ^* orbitals (anionic hyperconjugation or backbonding). The core 3d levels are not affected by such interactions and provide a calibration for assessing the magnitude of the hyper-

conjugation effect; that is, the effect of structural change on the ionization potentials is dissected into an inductive and a conjugative effect. Only the former affects the core levels, whereas both contribute to the lone-pair 5p levels. Hydrogen iodide, on the other hand, cannot contain hyperconjugative interactions. The displacement of this point from the line in Figure 2 thus indicates an average value of 0.14 eV for the hyperconjugative destabilization of iodine $5p_{1/2}$ electrons by alkyl groups. This relatively small effect is similar in magnitude to values calculated by Brogli and Heilbronner[7] using perturbation theory. There is the further implication in the fit of all of the alkyl iodides to a single line that the hyperconjugative interaction with C–C bonds must be approximately the same as with C–H bonds.

The present example demonstrates the unique advantages of using both valence shell and core photoelectron spectroscopy to elucidate the causes for chemical shifts of ionization potentials. We are continuing our studies of ionization potentials using these complementary techniques.

Stereochemical Course of a Gas-Phase Electrophilic Attack at Saturated Carbon. Reaction of meso-1,2-Dichloro-1,2-difluoroethane with Gaseous Brønsted Acids

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Abstract: The gas-phase electrophilic attack of He³H⁺ ions from the β decay of molecular tritium on meso-1,2-dichloro-1,2-difluoroethane leads to the predominant formation of a tritiated product retaining the original configuration of the substrate, with a considerably smaller yield of the tritiated dl form. The effect of the substrate pressure on the meso/dl ratio and the use of radiolytically produced methanonium and ethyl ions as milder gas-phase Brønsted acids show that the minor yield of the dl form is likely to arise from a racemization process, rather than from a discrete mode of attack, leading to inversion. The conclusion that the gas-phase tritiodeprotonation proceeds with retention of the substrate configuration is compared with the theoretical predictions on the course of the SE2 substitution processes.

The demonstration and the stereochemical study of a "pure" SE2 aliphatic substitution, i.e., the electrophilic attack at saturated carbon with no additional interaction between the electrophile and the leaving group, represent one of the most interesting problems in the field of electrophilic reactions. In fact, in contrast with the wealth of information on the correspondent nucleophilic processes, the study of SE2 reactions has been almost exclusively restricted to metal ions as the leaving groups, and the results have been deeply influenced by the availability of vacant orbitals in the metal atoms, leading to the possibility of "bridging" between the electrophile and the leaving group.[1]

The results recently obtained in the study of the gas-phase reactivity of an exceedingly strong Brønsted acid, the helium tritide ion from the β decay of ³H₂,[2–6] suggested the possibility of investigating a gas-phase electrophilic process, characterized by a simple and well de-

(1) For a comprehensive review, see F. R. Jensen and B. Rickborn, "Electrophilic Substitutions of Organomercurials," McGraw-Hill, New York, N. Y., 1968. Recently, however, examples of SE2 reactions involving the direct protonation of alkanes were reported by Olah and coworkers. See, e.g., G. A. Olah, G. Klopman, and R. H. Schlosberg, J. Amer. Chem. Soc., 91, 3261 (1969).

(2) F. Cacace and S. Caronna, ibid., 89, 6848 (1967).

(3) F. Cacace, R. Cipollini, and G. Ciranni, ibid., 90, 1122 (1968).

(4) F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, ibid., 90, 2222 (1968).

(5) F. Cacace, A. Guarino, and E. Possagno, ibid., 91, 3131 (1969).

(6) F. Cacace, A. Guarino, and M. Speranza, ibid., 93, 1088 (1971).

fined two-step mechanism, by the lack of the complicating effects of solvation, and whose "pure" SE2 character is ensured, *inter alia*, by the very nature of the electrophile.

It was therefore decided to undertake the study of the electrophilic attack of He^3H^+ ions from the β decay of molecular tritium on the meso form of 1,2-dichloro-1,2-difluoroethane, using a technique which has been recently the subject of a detailed review.[7]

The choice of the substrate was determined by its sufficient volatility, by the fact that the molecule contains only asymmetric carbons, and especially by the possibility of separating the meso from the *dl* form with a convenient and efficient gas chromatographic method.[8]

In order to evaluate the influence of the exothermicity of the electrophilic attack on the stereochemical course of the tritiodeprotonation, the investigation was extended to milder Brønsted acids, *i.e.*, the methanonium and the ethyl ions that can be conveniently prepared in the gas-phase with radiolytic techniques, and whose attack on a number of gaseous substrates has been extensively investigated with mass spectrometric and kinetic methods.[9]

Experimental Section

Materials. A sample of meso-1,2-dichloro-1,2-difluoroethane, kindly supplied to us by Professor Stöcklin of KFA, Jülich, was analyzed by vpc and its purity was found to exceed 99.1%.

The analytical conditions were the following: gas chromatograph, C. Erba, Model D, equipped with a thermal conductivity detector; column, copper, 15 m long, 3.5 mm i.d., packed with 20% β,β'-oxydipropionitrile on 60–80 mesh Chromosorb W, acid washed; temperature, 75°; carrier gas, He, at a flow rate of 1.8 l. hr^{-1}. Under these conditions, the retention times of the meso and the *dl* forms were 142 and 147 min, respectively.

The separation of the meso and *dl* forms in a commercial sample of 1,2-dichloro-1,2-difluoroethane from K & K Laboratories, Inc., was achieved by preparative vpc using the same technique. The analysis of the recovered samples showed no detectable impurities in the *dl* fraction and only a minor contamination of the meso fraction by the *dl* form.

The tritium gas was obtained from CEA, France, and its isotopic composition was checked by radio gas chromatography, using a 5-m Al_2O_3–Fe_2O_3 column[10] at −196°, in series with a flow proportional counter, according to a technique described elsewhere.[11]

Tritiated methane was purchased from the Radiochemical Centre (Amersham, England). The original sample, specific activity 100 mCi per mmol, was diluted with inactive methane and analyzed by radio gas chromatography using a 2-m, 5A molecular sieve column.

The O_2, CH_4, and the other gases used were research grade products from SIO (Milan) with a stated purity exceeding 99.9 mol % and were used without further purification.

Procedure. The reaction of meso-1,2-dichloro-1,2-difluoroethane with He^3H^+ was carried out by allowing a tracer amount of $^3H_2$ to decay at room temperature within sealed Pyrex bulbs containing variable amounts of the substrate and a small mole fraction of oxygen, used as a scavenger of thermal radicals.

After a storage period ranging from 144 to 165 days, the reaction vessels were opened and their contents diluted with precisely known amounts of meso- and *dl*-1,2-dichloro-1,2-difluoroethane.

(7) F. Cacace, *Advan. Phys. Org. Chem.*, **8**, 79 (1970).

(8) The separation technique was suggested to us by Professor G. Stöcklin, whose group subsequently described even more efficient gas chromatography methods. *Cf.* L. Vasàros, H. J. Machulla, and W. Tornau, *J. Chromatogr.*, **62**, 458 (1971).

(9) For a review, see F. H. Field, M. S. B. Munson, and D. A. Becker, *Advan. Chem. Ser.*, No. **58**, 167 (1966).

(10) H. A. Smith and E. H. Carter, "Tritium in the Physical and Biological Sciences," Vol. I, International Atomic Energy Agency, Vienna, 1962, p 121.

(11) G. Stöcklin, F. Cacace, and A. P. Wolf, *Z. Anal. Chem.*, **194**, 406 (1963).

After thorough mixing, the samples were subjected to a preparative gas chromatographic separation, using the 15-m β,β'-oxydipropionitrile column to resolve and purify the meso and the *dl* forms.

The recovered fraction containing the meso form was again diluted with the nonradioactive *dl* form and subjected to repeated separation and purification steps by preparative vpc, until a constant value of the specific activity of the meso form was reached. The same procedure was adopted for the purification of the radioactive *dl* fraction.

The absence of cross contamination in the meso and *dl* samples used for the final measurements was checked by analytical vpc, using the same β,β'-oxydipropionitrile column.

The reaction of meso-1,2-dichloro-1,2-difluoroethane with radiolytically formed ions was carried out within sealed Pyrex bulbs, containing a large excess of tritiated methane, a small concentration of oxygen, and the gaseous substrate at a pressure of 0.25 Torr, as shown in Table I.

Table I. Relative Yields of Tritiated *meso-* and *dl*-1,2-Dichloro-1,2-difluoroethane from the Attack of Radiolytically Produced $CH_4{}^3H^+$ and $C_2H_4{}^3{}^+H$ Ions on the Meso Form

Radiation dose, Mrads	Substrate pressure, Torr	Ratio of the meso to *dl* yields
7.5	0.25^a	3.37 ± 0.06
10	0.25	3.31 ± 0.06
11	0.25	3.32 ± 0.06

^{a} The system contained, in addition to the substrate, tritiated methane (25 mCi, 740 Torr) and O_2 (2.0–2.4 Torr).

The bulbs were irradiated with the ^{60}Co γ rays at 25°, in a 220 Gammacell from Atomic Energy Canada, Ltd. After receiving a dose between 7.5 and 11 Mrads, at a rate of *ca.* 0.2 Mrad hr^{-1}, the ampoules were opened and their content were analyzed according to the procedure described above.

Results and Discussion

Reaction of He^3H^+ Ions. The ratios of the yields of the tritiated meso and *dl* form from the gas-phase attack of He^3H^+ on meso-1,2-dichloro-1,2-difluoroethane at various pressures are given in Table II.

Table II. Relative Yields of Tritiated *meso-* and *dl*-1,2-Dichloro-1,2-difluoroethane from the Attack of He^3H^+ from the β Decay of $^3H_2$ on the Meso Form

Substrate pressure, Torr^a	Ratio of the meso to *dl* yield
3.6	2.33 ± 0.04
44.0	2.60 ± 0.04
147.0	2.80 ± 0.08

^{a} In addition to the substrate, the gaseous system contained $^3H_2$ (0.26 mCi) and O_2 (1–2 Torr).
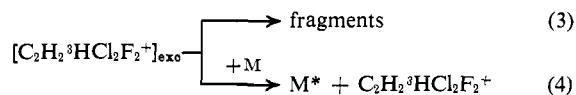
Because of the specific purpose of the investigation, only the tritiated products from the substitution of ^3H for H (tritiodeprotonation) were determined. The other products arising from the substitution of other atoms or groups and from the many fragmentation and condensation processes that are likely to occur in the system were disregarded. This limitation is clearly reflected in the comparatively low value of the *absolute* yield of the meso- and *dl*-1,2-dichloro-1,2-difluoroethane, whose combined activity was found to account for only *ca.* 1.2% of that contained in the He^3H^+ reagent formed in the system during the storage period from the β decay of molecular tritium (eq 1).

$$^3H_2 \longrightarrow He^3H^+ + \beta^- \qquad (1)$$
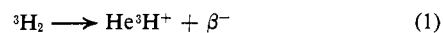
In agreement with the conclusion reached in previous studies,[2-7] it is suggested that the helium tritide ions attack the substrate according to a strongly exothermic triton transfer reaction (eq 2), yielding excited ions

$$He^3H^+ + C_2H_2Cl_2F_2 \longrightarrow He + [C_2H_2{}^3HCl_2F_2{}^+]_{exo} \quad (2)$$
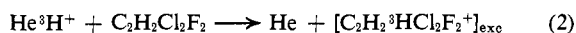
that can either decompose or undergo collisional stabilization in the organic gas (eq 3 and 4).

$$[C_2H_2{}^3HCl_2F_2{}^+]_{exo} \begin{cases} \longrightarrow fragments \quad (3) \\ +M \\ \longrightarrow M^* + C_2H_2{}^3HCl_2F_2{}^+ \quad (4) \end{cases}$$

It is suggested further that, among the many possible reaction channels, the stabilized ion interacts with the substrate, according to a fast, thermoneutral proton transfer process (eq 5) that represents a direct route to

$$C_2H_2{}^3HCl_2F_2{}^+ + C_2H_2Cl_2F_2 \longrightarrow C_2H^3HCl_2F_2 + C_2H_3Cl_2F_2{}^+ \quad (5)$$
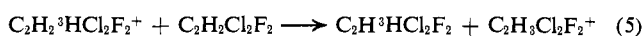
the observed dichlorodifluoroethane-³H.

Both steps of the mechanism suggested find close analogies with a number of processes studied in the gas phase, either by mass spectrometric or by kinetic methods. Apart from the reactions of the He³H⁺ ion with other substrates,[2-7] the attack of gaseous acids such as H₃⁺,[12,13] CH₅⁺, and C₂H₅⁺,[9] etc., on hydrocarbons alcohols,[14,15] esters,[16,17] alkyl halides,[18] etc., was in fact repeatedly shown to produce high yields of the corresponding protonated ions.

On the other hand, fast, thermoneutral proton transfer reactions analogous to process 5 were frequently observed in the ionic chemistry of gaseous hydrocarbons.[19] In particular, protonated alkyl halides were shown by ion-cyclotron resonance mass spectrometry to readily undergo proton transfer reactions to yield alkyl halides.[18]

The results of Table II show that the gas-phase tritiodeprotonation *leads predominantly to the formation of a labeled product which retains the original configuration of the substrate.*

However, the problem arises as to whether the smaller, yet significant, amount of the *dl* form is produced *via* an independent mode of attack, leading to inversion, or by the partial racemization of the excited intermediate I.

In the latter hypothesis, the yield of the *dl* form should depend, in the first place, on the rate of the racemization process, determined by the excitation level of the intermediate I and therefore by the exothermicity of the electrophilic attack, and, in the second place, on the lifetime of the excited intermediate before its quenching by process 4.

Effect of the Substrate Pressure. The small but real effect of the pressure on the meso/*dl* ratio occurs exactly in the direction expected on the grounds of the racemization hypothesis.

(12) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966).
(13) W. A. Chupka and E. Lindholm, *Ark. Fys.*, **25**, 349 (1965).
(14) V. Aquilanti, A. Galli, and G. G. Volpi, *Ric. Sci.*, **36**, 267 (1966).
(15) V. Aquilanti, A. Galli, and G. G. Volpi, *ibid.*, **37**, 244 (1967).
(16) H. Pritchard and A. G. Harrison, *J. Chem. Phys.*, **48**, 5623 (1968).
(17) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).
(18) See J. D. Baldeschwieder in "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1968, p 430.
(19) For a review, see P. Ausloos, S. G. Lias, and A. A. Scala, *Advan. Chem. Ser.*, No. **58**, 264 (1966).

In fact, a 40-fold decrease of the pressure, and therefore a corresponding increase in the lifetime of the excited species I before its quenching, was found to significantly increase the relative yield of the tritiated racemic products.

Triton Transfer from Methanonium and Ethyl Ions. An obvious test to clarify the crucial problem related to racemization was to measure the dependence of the meso/*dl* ratio on the excitation level of the intermediate I, *i.e.*, on the exothermicity of the triton transfer. The investigation was therefore extended to the reaction of the *meso*-1,2-dichloro-1,2-difluoroethane with two milder Brønsted acids whose attack is considerably less exothermic[20] than that in reaction 2. Methanonium and ethyl ions can be conveniently obtained in the gas-phase

$$CH_4{}^3H^+ + C_2H_2Cl_2F_2 \longrightarrow CH_4 + I \quad (6)$$

$$C_2H_4{}^3H^+ + C_2H_2Cl_2F_2 \longrightarrow C_2H_4 + I \quad (7)$$
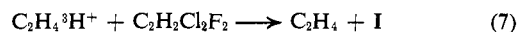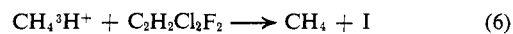
by the γ irradiation of methane, according to a technique introduced by Ausloos and coworkers,[19,21,22] and were extensively used as protonating reagents in kinetic[23] and mass spectrometric[9] studies.

It is now firmly established that the primary ionic species produced by the radiation from CH₄ undergo fast ion–molecule reactions leading to the formation of CH₅⁺ and C₂H₅⁺, which are unreactive toward CH₄ but efficiently protonate other compounds which may be present in the gas.

The reaction of the CH₄³H⁺ and C₂H₄³H⁺ ions from the γ radiolysis of tritiated methane, with a small concentration of *meso*-1,2-dichloro-1,2-difluoroethane in the presence of O₂ as a radical scavenger, gave both the meso and *dl* form in the ratios reported in Table I.

The results show that changing the electrophile from He³H⁺ to CH₄³H⁺ and C₂H₄³H⁺ caused a change of the meso/*dl* ratio that is surprisingly small, in view of the differences existing between the reagents, and in the reaction environment as well.

There is no doubt that several factors need to be considered in this connection. In the first place, the exothermicity of the triton transfer from He³H⁺ is higher by *ca.* 70 kcal mol⁻¹. In the second place, the lower concentration of the organic substrate in the experiments involving CH₄³H⁺ and C₂H₄³H⁺ ions (0.25 *vs.* at least 3.6 Torr) allows a longer lifetime of the haloalkanonium ion, before its quenching by reaction 5. Finally, the differences existing between the sterically unencumbered He³H⁺ ion and the more bulky methanonium or ethyl ions could conceivably affect the steric course of the electrophilic attack.

However, as a whole, the results of Table I support the view that the formation of the labeled *dl* form involves racemization of I, since the relative yield of the *dl* form shows a significant decrease as the exothermicity of the attack is substantially reduced in passing from reaction 2 to the considerably milder processes 6 and 7.

(20) The attack of CH₄³H⁺ is less exothermic than process 2 by *ca.* 70 kcal mol⁻¹. The ethyl ion is a still milder electrophile. See (a) F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **89**, 4272 (1967); (b) W. A. Chupka and M. E. Russel, *J. Chem. Phys.*, **49**, 5426 (1968).
(21) P. Ausloos, S. G. Lias, and R. Gorden, Jr., *ibid.*, **39**, 3341 (1963).
(22) P. Ausloos, S. G. Lias, and R. Gorden, Jr., *ibid.*, **40**, 1854 (1964).
(23) R. H. Lawrence, Jr., and R. F. Firestone, *J. Amer. Chem. Soc.*, **87**, 2288 (1965).

Conclusions

From the considerations outlined in the previous paragraphs, the conclusion can be drawn that the gas-phase tritiodeprotonation proceeds *via* a principal mechanism *which involves retention of configuration.* In fact, not only is the labeled meso form produced in a much higher yield, but the smaller amount of *dl* form is likely to arise *via* a racemization process, rather than an independent mode of attack leading to inversion. At this point, it seems appropriate to specifically state that no evidence is provided by the experimental results, nor is it suggested by us that the electrophilic attack takes place predominantly, or primarily, on the carbon atom or on the C–H bond, since, for instance, the formation of chloronium ions represents a very plausible, and perhaps predominant, mode of attack.[18] The present results indicate, however, that *those specific interactions, or the specific stage of the interaction, leading to formation of a bond between carbon and the incoming triton, proceed with retention of configuration.* The result provides direct experimental support to the view, long advanced on theoretical grounds but also somewhat controversial, that the electrophilic substitution at saturated carbon, a typical three-center, two-electron process, proceeds by frontside attack.[10,24,25]

This finding is of particular interest since it refers to a reaction occurring in the gas phase, free from the effects of solvation that considerably complicate similar processes occurring in solution.[26] Furthermore, the tritiodeprotonation involves an extremely simple reagent, perfectly defined from the structural and energetic point of view, whose very nature rules out the possibility of "bridging," or other complicating processes

that are frequently associated with the S_E2 processes in metal organic systems.

Finally, the observed retention of configuration provides some information on the structure of the substituted haloalkanonium ion that represents the precursor of the tritiated *meso*-1,2-dichloro-1,2-difluoroethane. While the trigonal bipyramidal structure a seems to be

ruled out, both the structures b, corresponding to the C_s symmetry proposed for the CH_5^+ ion,[27-34] and c, involving the triangular three-center bond proposed by Olah and coworker,[25] are related to a frontside electrophilic attack and do not conflict with the results of the present work.
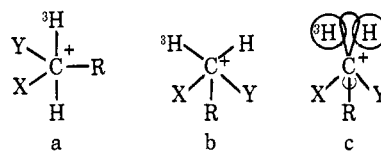
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