TABLE XIII

INFRARED SPECTRA OF $(CF_3)_2\overset{O}{P}\text{–}R$ COMPOUNDS[a]

Assignment	Cl	Br	CH_3	t-C_4H_9
CH_3, δ-a	...	...	1411vw	1470w
t-C_4H_9	...	...	...	1400vw 1270s
P=O, ν	1330s	1312s	1316s	1282s
c	1295m	1250w	...	...
c or CH_3, δ-e	...	...	1295w	...
C–F, ν	1204vs 1143s 1122m,sh 1098w	1202vs 1162s	1205vs 1180vs 1135vs 1098vw	1197vs 1172vs 1150s 1128s
...		1047w(?)		1026vw(?)
CH_3	...	...	887s	...
t-C_4H_9	...	...	...	812w
CF_3, δ-e	759m	753m	775m	745w
CH_3, ρ or P–CH_3, ν	...	...	732m	...
P–Cl, ν	615s	...	...	...
CF_3, δ-a	581sh 563s 536sh	ni	581sh 543m ...	ni
C–P–C, ν-a	498s	ni	495s	ni
C–P–C, ν-e (?)	...	ni	430m	ni

[a] All symbols are as in Table XII, and again the R groups (including Cl and Br) head the columns for the respective compounds.

comparisons in the pertinent range (1250–1350 cm.$^{-1}$); for the t-butyl phosphine oxide, however, the comparison could not be made for lack of the spectrum of the corresponding phosphine, t-C_4H_9-$P(CF_3)_2$.

The shift in the frequency of the P=O stretching band with substitution of groups or atoms on phosphorus has been used to calculate the effective electronegativity of the CF_3 group.[21] The result, 3.3 on the Pauling scale, seemed to be in the right range and its agreement with other spectral and thermochemical data also lent confidence. Thus we use the available data for POF_3, $POCl_3$, $POBr_3$ and $(CF_3)_3PO$ to derive the empirical equation $\nu = 918 + 41.3\Sigma x$ (where Σx is the sum of the electronegativity values for the groups attached to P=O and ν is the P=O stretching frequency) to determine the electronegativity of any group on phosphorus from the known values for the other groups. However, this equation was based upon compounds having C_{3v} symmetry and required testing for less symmetrical situations such as our new $(CF_3)_2P{=}O$ compounds, of symmetry no higher than C_s.

The calculated values shown in Table XIV are based upon the equation and our P=O stretching frequencies, using the accepted Pauling electronegativities for Cl and Br, and an x value for CH_3 calculated from the P=O stretching frequency in $(CH_3)_3PO$.[22]

TABLE XIV

CALCULATED ELECTRONEGATIVITIES OF THE CF_3 GROUP

Compound	$(CF_3)_2\overset{O}{P}Cl$	$(CF_3)_2\overset{O}{P}Br$	$(CF_3)_2\overset{O}{P}CH_3$
ν_{P-O} (cm.$^{-1}$)	1330	1312	1316
x calcd. for CF_3	3.5	3.4	3.6

Although these new electronegativity values for the CF_3 group, averaging 3.5, deviate appreciably from the value 3.3 given by Lagowski, the difference seems to be within the uncertainty of the electronegativity concept itself.[23]

[21] J. J. Lagowski, *Quart. Revs.* (London), **13**, 233 (1959).

[22] G. Goubeau and W. Berger, *Z. anorg. u. allgem. Chem.*, **304**, 147 (1960).

[23] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

An Electron Impact Study of 1,1,1-Trifluoroethane, 1,1,1-Trifluoropropane and 3,3,3-Trifluoropropene[1]

BY W. C. STEELE[2] AND F. G. A. STONE

RECEIVED FEBRUARY 10, 1962

The appearance potentials of the major positive ions in the mass spectra of 1,1,1-trifluoroethane, 1,1,1-trifluoropropane and 3,3,3-trifluoropropene have been measured. The R–CF_3 bond dissociation energy and the heat of formation are reported for each compound. The various processes for dissociation under electron impact are discussed.

In recent years the chemistry of organic fluorine compounds has been studied extensively. However, our knowledge of the thermochemistry[3] of these compounds has been somewhat limited by the experimental difficulties associated with calorimetric work. Another means of obtaining thermodynamic data is the electron impact method, which can lead directly to such important properties as bond dissociation energies and heats of formation.[4] An electron impact study of 1,1,1-trifluoroethane, 1,1,1-trifluoropropane and 3,3,3-trifluoropropene, undertaken in order to determine the effect of the CF_3 group on the thermodynamic properties of hydrocarbons, is described in this paper. The only previous electron impact investigation of small partially fluorinated hydrocarbons, containing more than one carbon atom, involved 1,1,1-trifluoroethane and hexafluoroethane.[5]

Experimental

The appearance potentials were measured using a Consolidated Electrodynamics Corporation Model 21-103 C mass spectrometer, modified to allow magnetic scanning. The data were evaluated from semilog plots of the ionization efficiency curves[6] when parallelism with the standard curve

---

[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[2] Postdoctoral Fellow, Harvard University.

[3] For a recent review see C. R. Patrick, "Advances in Fluorine Chemistry" (Eds. M. Stacey, J. C. Tatlow and A. G. Sharpe), **2**, 1 (1961), Butterworths, London.

[4] Mass spectrometry of fluorine compounds has recently been reviewed by J. R. Majer, *ibid.*, p. 55.

[5] V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Chem. Phys.*, **20**, 761 (1952).

[6] See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

was obtained. When the curves were not parallel the method[6] of extrapolated voltage differences was used and the results checked by a conventional extrapolation of the individual curves to zero intensity on linear paper. In each case argon (I = 15.76 e.v.) or krypton (I = 14.00 e.v.) was used as the standard and was introduced simultaneously with the sample. The samples were purified by gas chromatography prior to use.[7]

Results and Discussion

The appearance potentials of the ions measured for the three R–CF_3 compounds are listed in Table I, together with the relative abundances of the ions as calculated for a monoisotopic mass spectrum.

TABLE I

APPEARANCE POTENTIALS OF SOME R–CF_3 COMPOUNDS

m/e	Ion	Rel. ab. (%)	A_p(e.v.)
		CH_3CF_3	
69	CF_3^+	100	13.90 ± 0.03
65	$CH_3CF_2^+$	31.3	14.9 ± .2
64	$CH_2CF_2^+$	7.9	11.2 ± .1
45	CH_2CF^+	12.2	15.8 ± .2
33	CH_2F^+	9.8	15.6 ± .2
15	CH_3^+	11.8	15.0 ± .1
14	CH_2^+	4.6	16.2 ± .3
		$C_2H_3CF_3$	
96	$C_2H_3CF_3^+$	63.5	11.24 ± 0.04
95	$C_2H_2CF_3^+$	74.5	12.69 ± .05
77	$C_2H_3CF_2^+$	57.1	13.3 ± .15
76	$C_2H_2CF_2^+$	7.7	13.8 ± .1
75	$C_2HCF_2^+$	17.5	14.8 ± .2
69	CF_3^+	32.2	15.0 ± .2
51	CF_2H^+	34.1	14.9 ± .1
46	$C_2H_3F^+$	30.9	13.85 ± .02
27	$C_2H_3^+$	100	14.20 ± .05
26	$C_2H_2^+$	33.6	13.3 ± .15
		$C_2H_5CF_3$	
79	$C_2H_5CF_2^+$	10.6	14.9 ± 0.2
78	$C_2H_4CF_2^+$	4.6	12.53 ± .04
77	$C_2H_3CF_2^+$	9.3	13.6 ± .1
69	CF_3^+	8.7	14.8 ± .1
59	$C_2H_4CF^+$	5.6	15.8 ± .1
51	CF_2H^+	13.3	15.9 ± .1
33	CH_2F^+	4.7	15.7 ± .3
29	$C_2H_5^+$	100	12.82 ± .02
28	$C_2H_4^+$	<5.3	13.0 ± .2
27	$C_2H_3^+$	35.3	15.3 ± .1

The two saturated compounds, 1,1,1-trifluoroethane and 1,1,1-trifluoropropane, possessed parent peaks of such low intensity that measurement of their ionization potentials was not possible, as is the case with the perfluoroalkanes.[8] However, 3,3,3-trifluoropropene had an intense parent peak, and its ionization potential was measured as 11.24 ± 0.04 e.v. This result is about 0.7 e.v. higher than the ionization potential of ethylene. In both cases ionization is accomplished by removal of an electron from the π-system of the carbon–carbon double bond; the larger value for the fluorocompound can be ascribed to the electronegativity of the CF_3 group.[9]

The appearance potential of an R_1^+ ion formed from an R_1R_2 molecule by the process

$$R_1R_2 + e \longrightarrow R_1^+ + R_2 + 2e \qquad (1)$$

can be written either as

$$A_p(R_1^+) = I(R_1) + D(R_1 - R_2) \qquad (2)$$

or

$$A_p(R_1^+) = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2) \quad (3)$$

with the important restriction that the fragments must be formed essentially at rest and in their ground states. When used in conjunction with appropriate auxiliary data, appearance potentials can lead to the dissociation energies D of R_1–R_2 bonds, or to one of the several heats of formation of equation 3. Equation 2 can be applied directly to calculation of the R–CF_3 bond dissociation energies, since the ionization potentials of the hydrocarbon radicals and of CF_3 have been measured directly by electron impact.[10] Heats of formation of alkyl ions and radicals are well known, and in this paper are taken from a recent tabulation,[11] while values for other ions are taken from the tables of Field and Franklin,[6] unless specified otherwise.

The ionization potentials and heats of formation of the vinyl and the trifluoromethyl radicals, and the heats of formation of their ions, which are important in the interpretation of the work described in this paper, require further comment. The ionization potential of the vinyl radical has been measured directly as 9.45 e.v.[10b] The appearance potential of the vinyl ion from ethylene has also been determined, leading to the calculated values $\Delta H_f(C_2H_3^+)$ = 283 kcal. mole^{-1} and $\Delta H_f(C_2H_3\cdot)$ = 65 kcal. mole^{-1}. However, the appearance potential of $C_2H_3^+$ from propylene[6] can be used with the above value for $I(C_2H_3\cdot)$ to give $\Delta H_f(C_2H_3^+)$ = 289 kcal. mole^{-1} and $\Delta H_f(C_2H_3\cdot)$ = 71 kcal. mole^{-1}. The latter values are in fact the same as those listed by Wallenstein and Krauss.[11] In this paper the average values $\Delta H_f(C_2H_3^+)$ = 286 kcal. mole^{-1} are $\Delta H_f(C_2H_3\cdot)$ = 68 kcal. mole^{-1} are used.[12]

The ionization potential (10.15 e.v.) of the trifluoromethyl radical has been measured directly[10a] and the result confirmed.[13] However, when this result is used in conjunction with other appearance potential data to determine bond dissociation energies, the values obtained lack consistency. Thus, although the carbon–hydrogen bond dissociation energy calculated for fluoroform[14] is in excellent agreement with the value obtained from

---

[7] We are indebted to Mr. J. R. Phillips of this Laboratory for preparing the gases.

[8] F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Standards*, **49**, 343 (1952).

[9] R. Bralsford, P. V. Harris and W. C. Price, *Proc. Roy. Soc.* (London), **258**, 459 (1960).

[10] (a) F. P. Lossing, *Ann. N. Y. Acad. Sci.*, **67**, 499 (1957); F. P. Lossing, P. Kebarle and J. B. DeSousa, "Adv. Mass Spectrometry" (Ed., J. D. Waldron), Pergamon Press, London, 1959; and references cited therein. (b) A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 519 (1960).

[11] M. L. Wallenstein and M. Krauss, *J. Chem. Phys.*, **34**, 929 (1961).

[12] An electron impact study of neopentane (F. W. Lampe and F. H. Field, *J. Am. Chem. Soc.*, **81**, 3238 (1959)) has led to this same result.

[13] R. I. Reed and W. Snedden, *Trans. Faraday Soc.*, **54**, 301 (1958).

[14] J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

kinetic data,[15] the carbon–halogen bond dissociation energies predicted[16,17] for the trifluorohalomethanes are considerably less than expected on the basis of other work. Indeed, the electron impact studies of the trifluorohalomethanes[16,17] have led to a proposed value for $I(CF_3\cdot)$ of 9.3 e.v. Furthermore, with one exception, there seems to be no consistent relationship between experimental heats of formation of compounds containing trifluoromethyl groups and the CF_3^+ appearance potentials. The exception is provided by the heats of formation[18] of carbon tetrafluoride and fluoroform which can be used in conjunction with the appearance potentials[18] of their CF_3^+ ions to give $\Delta H_f(CF_3^+) = 119.4$ and 120.4 kcal. mole^{-1}, respectively. In view of this agreement, plus the agreement between kinetic and electron impact values for $D(F_3C\text{-}H)$, the values of $I(CF_3\cdot) = 10.1_5$ e.v. and $\Delta H_f(CF_3^+) = 120$ kcal. mole^{-1}, and the resulting $\Delta H_f(CF_3\cdot) = -114$ kcal. mole^{-1}, are used in this paper as the best values currently available.

The semilog appearance potential curves for the CF_3^+ ion from 1,1,1-trifluoroethane[19] and the $C_2H_5^+$ ion from 1,1,1-trifluoropropane are parallel to the rare gas curves over the lower portions of the curve. The $C_2H_3^+$ ion from the propene $CF_3CH{:}CH_2$ shows the slight departure from parallelism noted for this ion from ethylene[10b] and vinylboron difluoride.[20] As a result of the formation of these ions by apparently simple processes, the $R\text{–}CF_3$ bond dissociation energies (Table II) have been calculated directly from the appearance potentials of the ions and the appropriate free radical ionization potentials. In each case, the ion formed from the opposing group shows some degree of tailing, a phenomenon frequently associated with the presence of excess energy.[21] In confirmation of this, bond energies calculated from the appearance potentials of these ions result in higher values than those obtained above for 1,1,1-trifluoroethane and 1,1,1-trifluoropropane. However, the CF_3^+ ion from 3,3,3-trifluoropropene gives an $R\text{–}CF_3$ bond energy which is equal, to within experimental error, to the value derived from the $C_2H_3^+$ ion. This result may be taken as confirmation of the choice for $I(CF_3\cdot)$, although it is just possible that the agreement is fortuitous.

The calculated $R\text{–}CF_3$ bond dissociation energies are somewhat higher than those for the corresponding $R\text{–}CH_3$ compounds. Values of 88, 94 and 109 kcal. mole^{-1} for $R\text{–}CF_3$ ($R = CH_3$, C_2H_5 and C_2H_3, respectively) are to be compared with 84.6, 81.0 and 95.3 kcal. mole^{-1} for the respective hydrocarbons.[22] Such a trend in the $R_1\text{–}R_2$ bond dissociation energies seems quite reasonable. The elevation in carbon–carbon bond energy in 1,1,1-trifluoroethane over that in ethane may be correlated with the observed shortening[23] of the carbon–carbon bond length in 1,1,1-trifluoroethane. Moreover, the increase in D in changing from sp^3 to sp^2 hybridized carbon atoms is comparable in the two series. It is also interesting that the carbon–carbon bond dissociation energies are very similar in CH_3CN (103 kcal. mole^{-1})[24] and in CF_3CN (100 kcal. mole^{-1}, using $I(CF_3\cdot) = 10.1_5$),[25] molecules in which the carbon–carbon bond lengths[23] are about equal, but shorter than those of both ethanes. However, without proof of absence of kinetic energy effects these values should be considered as upper limits.

In view of the previously mentioned difficulties associated with experimental determination of heats of formation of fluorinated organic compounds, it seemed worthwhile to derive these from the appearance potentials of the ions used in the $R\text{–}CF_3$ bond energy (Table II) calculations. It is difficult to assess the reliability of these results, since the calculations rest not only on the assumption that no excess energy is present in the dissociation process, but also on the choice of heats of formation of the trifluoromethyl and vinyl radicals and ions. It is to be noted, however, that the use of these values is generally successful in predicting the appearance potentials of the other dissociation processes, as is shown below. It may be mentioned in passing that the heats of formation of 3,3,-3-trifluoropropene and 1,1,1-trifluoropropane lead directly to a value (−30 kcal. mole^{-1}) for the heat of hydrogenation of 3,3,3-trifluoropropene. This may be compared with the heats of hydrogenation of ethylene (−32.7 kcal. mole^{-1})[22] and propylene (−29.7 kcal. mole^{-1}),[22] but the degree of accuracy available here does not warrant a discussion of the effect of the CF_3 group on the heat of hydrogenation of ethylene based on this result alone.

TABLE II

BOND DISSOCIATION ENERGIES AND HEATS OF FORMATION

Compound $R\text{–}CF_3$	$I(R)$ (e.v.)	$D(R\text{–}CF_3)$ (kcal. mole^{-1})	$\Delta H_f(R\text{–}CF_3)$ (kcal. mole^{-1})
CH_3CF_3	10.1_5[a]	88	−169
$C_2H_5CF_3$	8.7_2[b]	94	−185
$C_2H_3CF_3$	9.4_5[c]	109	−155

[a] $I(CF_3\cdot)$. [b] From ref. 10a. [c] From ref. 10b.

It has been shown for a group of related molecules, $R\text{–}BF_2$, that the ion formed by loss of both H and BF_2 is accompanied by the formation of an HBF_2 molecule.[20] This process is very important in the mass spectra of the organoboron difluorides. That the analogous process is less important in the $R\text{–}CF_3$ series is evident from comparison of the relative peak heights of $C_2H_4^+$ and $C_2H_5^+$ for the R = ethyl compounds in the two series, for example. This result is not surprising when the differing

---

(15) G. O. Pritchard, H. O. Pritchard, H. I. Schiff and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).

(16) V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Res. Natl. Bur. Standards*, **57**, 113 (1956).

(17) J. Marriott and J. D. Craggs, *J. Electron Control*, **1**, 405 (1956).

(18) See ref. 3, and references cited therein.

(19) Values obtained in this Laboratory for $A_p(CF_3^+)$ and $A_p(CH_3^+)$ from 1,1,1-trifluoroethane agree satisfactorily with the earlier values of 14.0 e.v. and 15.2 e.v. obtained by Dibeler, *et al.*[5]

(20) W. C. Steele, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 1154 (1962).

(21) J. A. Morrison, *Revs. Pure and Applied Chem.*, **5**, 22 (1955).

(22) Calculated from the free radical heats of formation and/or heats of formation of the hydrocarbons taken from F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

(23) See L. E. Sutton, *Tetrahedron*, **5**, 118 (1959), for a tabulation of C–C bond lengths in CH_3- and CF_3-compounds.

(24) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

(25) G. P. Van der Kelen and P. J. DeBievre, *Bull. soc. chim. Belg.*, **69**, 379 (1960).

natures of the bonded BF_2 and CF_3 groups are considered. The boron atom in the RBF_2 compound has available a potentially empty *p*-orbital which might accept a hydrogen atom from the R group in the activated RBF_2^+ parent ion, facilitating formation of HBF_2 upon subsequent rupture of the carbon–boron bond. No such orbital is available from the CF_3 group, necessitating the simultaneous breaking of two bonds and formation of a third upon decomposition of the activated parent ion if the HCF_3 molecule is to be formed. However, it can be shown that this pathway for decomposition is followed in the R–CF_3 series. In the case of 3,3,3-trifluoropropene, the $C_2H_2^+$ ion can be formed either by

$$C_2H_3CF_3 + e \longrightarrow C_2H_2^+ + H + CF_3 + 2e \quad (4)$$

or

$$C_2H_3CF_3 + e \longrightarrow C_2H_2^+ + HCF_3 + 2e \quad (5)$$

Calculated appearance potentials, using ΔH_f-(HCF_3) = -162.6 kcal. mole^{-1}.[18] are 17.7_8 e.v. and 13.4_0 e.v. for processes 4 and 5, respectively. The experimentally observed value of 13.3 ± 0.15 e.v. confirms process 5. The calculation is less successful for the other two compounds. For 1,1,1-trifluoropropane the calculated values are 16.3 e.v. and 11.9 e.v., compared with the experimental 13.0 e.v., and for 1,1,1-trifluoroethane 19.0 e.v. and 14.7 e.v., respectively, compared with an observed 16.2 e.v. In both cases, however, the observed value is much lower than the value calculated for a process of type 4, indicating that a reaction of type 5 must be the one taking place.

The only instance in which identical hydrocarbon ions from two compounds have been observed is the vinyl ion from both the trifluoropropene and the trifluoropropane. In the former case, the appearance potential has been used in calculating the bond dissociation energy and the heat of formation. In the latter case, the ion may be formed by two processes of nearly equal energy

$$C_2H_5CF_3 + e \longrightarrow C_2H_3^+ + H_2 + CF_3 + 2e \quad (6)$$

and

$$C_2H_5CF_3 + e \longrightarrow C_2H_3^+ + H + HCF_3 + 2e \quad (7)$$

Calculated appearance potentials are 15.4_8 e.v. and 15.6_1 e.v., respectively. The observed value of 15.3 ± 0.1 e.v., although slightly lower than the calculated values, is in reasonable agreement.

Another example of the elimination of a molecule during the dissociation process involves the loss of hydrogen fluoride from the parent molecule ion. For 1,1,1-trifluoroethane the two lowest energy processes for formation of the $C_2H_2F_2^+$ ion are

$$CH_3CF_3 + e \longrightarrow C_2H_2F_2^+ + HF + 2e \quad (8)$$

and

$$CH_3CF_3 + e \longrightarrow C_2H_2F_2^+ + H + F^- + e \quad (9)$$

Appearance potentials of 11.4_5 e.v. and 13.7_0 e.v. can be calculated for processes 8 and 9, respectively, using the ionization potential[9] and the heat of formation[18] of 1,1-difluoroethylene to obtain the heat of formation of the $C_2H_2F_2^+$ ion. The observed appearance potential of 11.2 e.v. confirms process 8.[26] Lack of appropriate data precludes a similar calculation for the other two R–CF_3 compounds. Loss of HX from monohalogenated ethanes by a similar process has been observed by Collin[27] and by Irsa.[28]

Among the more interesting phenomena to be observed in a mass spectrum is the presence of ions formed by rearrangement of atoms to give positive ions which cannot be formed by simple bond rupture. Such rearrangement peaks often stand out graphically in the mass spectra of halogenated materials and frequently are present in such large relative abundances as to confuse attempts at molecular structure determination.[29] Several such ions are present in the mass spectra of the R–CF_3 compounds: notably CH_2F^+ and CHF_2^+ in all three spectra, and $C_2H_3F^+$ in the spectrum of 3,3,3-trifluoropropene. The ion CF_2H^+ from 1,1,-1-trifluoroethane and the ion CH_2F^+ from 3,3,3-trifluoropropene are present in quantities too small to permit appearance potential measurement, but values are recorded for the other cases (Table I). It is interesting to speculate concerning the mechanism of rearrangement but, unfortunately, the thermodynamic data required for any calculation are available in only one instance. Two possible processes for the formation of CF_2H^+ from 3,3,3-trifluoropropene are

$$C_2H_3CF_3 + e \longrightarrow CF_2H^+ + C_2H_2F + 2e \quad (10)$$

and

$$C_2H_3CF_3 + e \longrightarrow CF_2H^+ + F + C_2H_2 + 2e \quad (11)$$

If process 11 is thought of as proceeding through the CF_3H^+ ion as an intermediate, then the appearance potential (15.6 e.v.)[30] of the CF_2H^+ ion from fluoroform may be used to calculate an appearance potential for (11), assuming the hydrocarbon fragment is acetylene. The value thus obtained (17.6 e.v.) is much higher than that observed (14.9 e.v.). The appearance potential for process 10 should be lower than that for (11) by an amount equal to the C–F bond strength in the C_2H_2F radical. It seems likely, therefore, that rearrangement takes place by interchange of hydrogen and fluorine atoms prior to decomposition of the activated parent ion, giving rise to the products shown for reaction 10.

The $C_2H_3F^+$ ion from 3,3,3-trifluoropropene is the only example in this work of a rearrangement peak formed by simple transfer of an atom without displacement of a second atom.[31] The appearance potential (13.8_5 e.v.) of $C_2H_3F^+$ is only 3.48 e.v. (80 kcal. mole^{-1}) above the ionization potential[9] of vinyl fluoride. Since a 109 kcal. mole^{-1} carbon–carbon bond (Table II) must be broken in the process, this requires that $D(C_2H_3\text{–}F)$ be 29 kcal. mole^{-1} greater than $D(F_2C\text{–}F)$. If $\Delta H_f(CF_3\cdot) = -114$ kcal. mole^{-1} and $\Delta H_f(CF_2\cdot) = -36$ kcal. mole^{-1},[32] then $D(F_2C\text{–}F) = 97$ kcal. mole^{-1}, leading to $D(C_2H_3\text{–}F) = 126$ kcal. mole^{-1}. This latter value constitutes a reasonable estimate for

---

(26) Absence of negative ions in the mass spectrum of 1,1,1-trifluoroethane has been reported by R. M. Reese, V. H. Dibeler and F. L. Mohler. *J. Res. Natl. Bur. Standards*, **57**, 367 (1956).

(27) J. Collin, *Bull. soc. roy. sci. Liège*, **25**, 426 (1956).

(28) A. P. Irsa, *J. Chem. Phys.*, **26**, 18 (1957).

(29) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(30) W. C. Steele, unpublished work.

(31) For example, no $C_2H_5F^+$ ion is observed in the mass spectrum of 1,1,1-trifluoropropane.

(32) L. Brewer, J. L. Margrave, R. F. Porter and K. Wieland, *J. Phys. Chem.*, **65**, 1913 (1961).

the carbon–fluorine bond dissociation energy in vinyl fluoride, representing a rise of 19 kcal. mole^{-1} in carbon–fluorine bond energy in changing from sp^3 hybridized carbon in methyl fluoride to sp^2 hybridized carbon in vinyl fluoride. This also serves to illustrate that the rearrangement process leading to formation of $C_2H_3F^+$ proceeds with only a small, if not zero, activation energy.

Ions produced by loss of fluorine from the parent ion give peaks which are intense in all three spectra. These ions can be formed either by loss of a neutral fluorine atom or by a pair production process involving formation of a negative F^- ion. The relatively high appearance potentials for these ions indicate the former process as the more likely and, in fact, the appearance potential curve for $C_2H_5CF_2^+$ from 1,1,1-trifluoropropane shows an indication of divergence to a lower value at the foot of the curve. Unfortunately, the very low intensity at this point makes it impossible to locate the lower limit. In only one case was it possible to measure a checking value: the $C_2H_3CF_2^+$ ion has been measured for both 3,3,3-trifluoropropene and 1,1,1-trifluoropropane. The appearance potential of the ion from the two sources can be correlated by assuming these two processes for formation

$$C_2H_3CF_3 + e \longrightarrow C_2H_3CF_2^+ + F + 2e \quad (12)$$

and

$$C_2H_5CF_3 + e \longrightarrow C_2H_3CF_2^+ + HF + H + 2e \quad (13)$$

Assuming (12), the calculated appearance potential for (13) is 13.2$_5$ e.v., compared to the observed 13.6 e.v. No other combination of the many possible processes predicts the appearance potential to better than 1.0 e.v. These results indicate that negative ion formation does not play an important role in the decomposition by electron impact of the three fluorocarbons examined in this study.[26]

It is evident from the foregoing discussion that the values chosen for the heats of formation of the trifluoromethyl radical and its positive ion lead to heats of formation of the R–CF_3 compounds which satisfactorily interpret the appearance potentials of many of the positive ions. Processes 5, 6, 7 and 8 are cases where the correct process is unambiguous and the appearance potentials can be calculated with some accuracy. In all four of these cases the calculated value is somewhat above that observed but only by a few kcal. mole^{-1}. A slightly better fit might be obtained by taking $\Delta H_f(CF_3^+)$ = 127 kcal. mole^{-1} and $\Delta H_f(CF_3\cdot)$ = -107 kcal. mole^{-1}, but the present results alone do not warrant this change.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, HARVARD MEDICAL SCHOOL, AND THE CANCER RESEARCH INSTITUTE OF THE NEW ENGLAND DEACONESS HOSPITAL, BOSTON, MASSACHUSETTS]

The Elbs Peroxydisulfate Oxidation: Kinetics[1]

BY E. J. BEHRMAN AND PAMELA P. WALKER

RECEIVED MARCH 15, 1962

The reaction of persulfate ion with 2-hydroxypyridine and *o*-nitrophenol has been studied. The kinetics are first order in both persulfate and phenolate ion. There is a general and positive salt effect and no inhibition by the sulfate radical trapping agent, allyl acetate. A bimolecular reaction of persulfate and the phenolate ions is postulated, while heterolysis or homolysis of persulfate prior to attack by the phenolate ion is considered unlikely.

K. Elbs reported in 1893 that the reaction of *o*-nitrophenol in alkaline solution with persulfate[2] yielded 2,5-dihydroxynitrobenzene (nitroquinol) after subsequent heating in acid solution.[3] Later it was found[4] that the initial product in the reaction was a *p*-hydroxyaryl sulfate which could be cleaved by acid hydrolysis to yield the dihydroxy compound. The reaction has since been extended to include a large number of phenols. The position *para* to the existing phenolic group is substituted preferentially but not exclusively; *ortho*-substitution has been detected in a number of cases.[5,6] *Ortho*-substitution is exclusive when the *para*-position is blocked; no case of *meta*-substitution has been reported. Sethna[7] has reviewed the literature through 1950 and, since that time, a few papers have appeared.[6,8] The extension of this reaction to aromatic amines[9] merits particular mention. It should be noted that in this latter case the substitution is preferentially *ortho*.

The mechanism of the reaction has not been investigated. Baker and Brown[10] postulated an attack on the phenolate ion by the sulfate radical. This hypothesis is supported only indirectly by the fact that persulfate is known to be able to decompose *via* a free radical route[11] and by the fact that coupling products have been found as products of the reaction of persulfate with phenols and aromatic amines.[9e,12]

---

[1] This investigation was supported by United States Public Health Service Grant A567 and by United States Atomic Energy Commission Contract AT(30-1)-901 with the New England Deaconess Hospital.

[2] Persulfate = peroxydisulfate = peroxodisulfate. See footnote 4 of ref. 22.

[3] K. Elbs, *J. prakt. Chem.*, **48** [156], 179 (1893).

[4] German Patent 81,068. From P. Friedlaender, *Fortschritte der Theerfarbenfabrikation*, 4th part, 1894–7, p. 126.

[5] J. Forrest and V. Petrow, *J. Chem. Soc.*, 2340 (1950).

[6] E. J. Behrman and B. M. Pitt, *J. Am. Chem. Soc.*, **80**, 3717 (1958).

[7] S. M. Sethna, *Chem. Revs.*, **49**, 91 (1951).

[8] (a) R. U. Schock, Jr., and D. L. Tabern, *J. Org. Chem.*, **16**, 1772 (1951). (b) K. Babu Rao and N. U. Subba Rao, *J. Sci. Ind. Res.*, **14B**, 130 (1955). From *Chem. Abs.*, **49**, 10877 (1955). (c) C. E. Dalgliesh and W. Kelly, *J. Chem. Soc.*, 3726 (1958).

[9] (a) E. Boyland, D. Manson and P. Sims, *ibid.*, 3623 (1953). (b) E. Boyland and P. Sims, *ibid.*, 980 (1954). (c) E. Boyland, P. Sims and D. C. Williams, *Biochem. J.*, **62**, 546 (1956). (d) P. Sims, *J. Chem. Soc.*, 44 (1958). (e) E. Boyland and P. Sims, *ibid.*, 4198 (1958).

[10] W. Baker and N. C. Brown, *ibid.*, 2303 (1948).

[11] I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).

[12] R. G. R. Bacon, R. Grime and D. J. Munro, *J. Chem. Soc.*, 2275 (1954).