bonyl group, a disulfide group or a double-bonded sulfur (*e.g.*, thiourea) has also been noted in pulse-radiolysis studies.[29] In each case our esr data provide more specific information concerning how the electron attaches to these molecules.

Considerable interest attaches to the study of radiation effects on disulfide bonds because of their essential role in determining the tertiary structure of protein. An early hypothesis was that the disulfide bond was particularly susceptible to radiation damage because of hole transfer to that bond.[30] On the other hand, it has been suggested that because of their high reactivity with the solvated electron the disulfide bonds in certain protein such as ribonuclease can account for most of the proteins reactivity in irradiated aqueous solutions.[31] Our esr results obtained on small molecules, showing that disulfide bonds are favored sites for trapping holes and for electron attachment, tend to support both the foregoing suggestions.

*Acknowledgment.* This work was supported by Contract AT(30-1) 3558 with the Atomic Energy Commission and Public Health Grant RH 00450.

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(30) W. Gordy, W. B. Ard, and H. Shields, *Proc. Natl. Acad. Sci.*, *U. S.*, **41**, 983 (1955).

(31) M. Ebert and A. J. Swallow, "Solvated Electron" Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 289.

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# Positive and Negative Ion Formation In Hexafluoroacetone by Electron Impact

**by P. Harland and J. C. J. Thynne**

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Positive and negative ion formation as a result of the electron bombardment of hexafluoroacetone has been studied and, from the positive ion data, a value of $\leq 4.16$ eV calculated for the bond dissociation energy $D(CF_3-COCF_3)$. Hexafluoroacetone is an abundant source of negative ions, the principal ions being $CF_3COCF_3^-$, $CF_3COCF_2^-$, $(CF_3)_2C^-$, $CF_3CO^-$, $CF_3^-$, $CF_2^-$, $CFO^-$ and $F^-$. The dependence of their formation upon electron energy has been studied and a deconvolution method used to analyze the results; ionization processes have been suggested to account for the formation of most of these ions at low electron energies and electron affinities calculated for several species. $CF_3COCF_3^-$ is formed as a result of both primary and secondary electron capture and a value of $0.61 \times 10^{-16}$ cm$^2$ has been calculated for the electron attachment cross section for the ketone.

## Introduction

Electron bombardment of a molecule may result in the formation of positive and negative ions.[1] The latter may be produced by (i) resonance attachment $AB + e \rightarrow AB^-$; (ii) dissociative resonance capture, $AB + e \rightarrow A^- + B$; or (iii) ion-pair formation; $AB + e \rightarrow A^- + B^+ + e$.

These mechanisms usually operate at different electron energies, the resonance processes usually occurring in the 0–10 eV energy region and the ion-pair processes at energies above this.

We have examined positive and negative ion formation in hexafluoroacetone over the energy range 0–70 eV. This compound was chosen because appearance potential studies of positive ions should yield information regarding the carbon–carbon bond strength and enable comparison to be made with the analogous bond strength in acetone; in addition, preliminary studies showed several negative ions to be formed and we have examined some of these ions and their electron energy dependence.

In electron impact studies, when the source of the electrons is a heated filament, uncertainties arise in the interpretation of the experimental ionization data because of the energy spread of the thermionically-emitted electron beam. This is because the ionization thresholds become smeared-out as a result of the high-energy tail of the electron energy distribution. Morrison[2]

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(1) H. S. W. Massey, "Negative Ions," Cambridge University Press, London, 1950.

(2) J. D. Morrison, *J. Chem. Phys.*, **39**, 200 (1963).

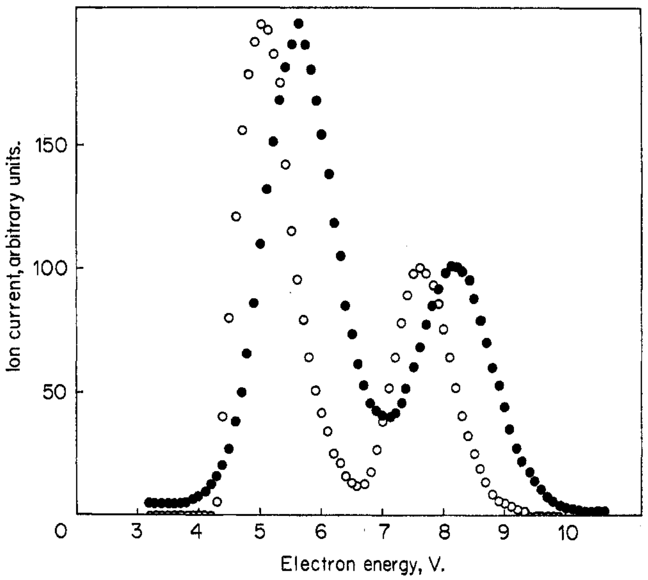

Figure 1. Ionization efficiency curve for $O^-$ ion formation by $SO_2$. Full circles, original experimental data; open circles, deconvoluted results obtained using 15 smoothing and 20 unfolding iterations.

has used analytical methods to remove the energy spread and has applied the technique to the problem of positive ions. We have applied such methods to study negative ion formation at low electron energies[3] and have extended their use in this work to include hexafluoroacetone.

## Experimental Section

The data were obtained using a Bendix time-of-flight mass spectrometer, Model 3015. The pressure in the ion source was usually maintained below $5 \times 10^{-6}$ mm in order to reduce the possibility of ion formation due to ion–molecule reactions. The energy of the ionizing electrons was read on a Solartron digital voltmeter, Model LM 1619, and the spectra recorded on a 1-mV Kent potentiometric recorder.

In both the positive and negative ion studies, the electron current was maintained constant by automatic regulation over the whole energy range investigated. Ionization curves were usually measured three to five times, the appearance potentials for negative ions being reproducible to ± 0.1 eV.

The appearance potential of the $O^-$ ion from $SO_2$ was used as the reference for electron energy scale calibration.[3-5] In a previous paper[6] we used the $S^-$ ion from $CS_2$ for scale calibration purposes; this is a satisfactory calibrant but we now find the $O^-$ ion formed by $SO_2$ to be superior. Our principal reasons are that the $O^-$ ion is a more intense ion and also (as can be seen in Figure 1) two resonance peaks are observed for the $O^-$ ion. As a consequence, although the appearance potential of the ion at 4.2 eV is chosen for calibration purposes, the second appearance potential (6.6 eV), the positions of the peak maxima (4.9 and 7.5 eV) and the energy differences between these peak parameters serve as checks on the reliability of the calibration. For positive ion studies, argon was used to calibrate the energy scale, the method used for determining the appearance potentials being the semilogarithmic plot technique.

The electron energy distribution, which was required to be known for the deconvolution procedure, was measured using the $SF_6^-$ ion formed by sulfur hexafluoride.[7,8] It was found that performing 15 smoothing and 20 unfolding iterations on the basic experimental data enabled satisfactory evaluation of appearance potentials, resonance peak maxima and peak widths (at half-height) to be made.

*Materials.* Hexafluoroacetone was obtained by dehydration of the sesquihydrate. The impurities were fluoroform, hexafluoroethane, and carbon dioxide and these were removed by prolonged pumping on a vacuum line at −130°.

## Results and Discussion

(*a*) *Positive Ion Formation.* We have measured the appearance potentials of the $CF_3^+$ and $CF_3CO^+$ ions formed from hexafluoroacetone and obtained $A(CF_3^+) = 14.26 \pm 0.10$ eV, and $A(CF_3CO^+) = 12.04 \pm 0.12$ eV.

If the ionization processes leading the formation of these ions correspond to

$$CF_3COCF_3 + e \longrightarrow CF_3^+ + COCF_3 + 2e \quad (1)$$

$$\longrightarrow CF_3CO^+ + CF_3 + 2e \quad (2)$$

then we may use these results to evaluate the strength of the $CF_3$–$COCF_3$ bond by means of such relations as $D(CF_3\text{–}COCF_3) \leqslant A(CF_3^+) - I(CF_3)$, where $I(CF_3)$ refers to the ionization potential of the trifluoromethyl radical.

$I(CF_3)$ has been measured directly by electron impact by two groups of workers[9,10] and a value of 10.1 eV obtained. It has been suggested,[11] on the basis of reasonable values for the carbon–halogen bond strength in the trifluoromethyl halides, that this measured ionization potential is too high by about 0.8 eV.

Recently, Lifschitz and Chupka[12] have measured the

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(3) K. A. G. MacNeil and J. C. J. Thynne, *Int. J. Mass Spectrom.*, **3**, 35 (1969).

(4) K. Kraus, *Z. Naturforsch.*, **16a**, 1378 (1961).

(5) J. G. Dillard and J. L. Franklin, *J. Chem. Phys.*, **48**, 2349 (1968).

(6) J. C. J. Thynne, *J. Phys. Chem.*, **73**, 1586 (1969).

(7) W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

(8) G. J. Schulz, *J. Appl. Phys.*, **31**, 1134 (1960).

(9) J. B. Farmer, I. H. S. Henderson, and F. P. Lossing, *J. Chem. Phys.*, **23**, 403 (1955).

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

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

(12) C. Lifschitz and W. A. Chupka, *J. Chem. Phys.*, **47**, 3439 (1967).

ionization potential for the trifluoromethyl radical by a photoionization technique and have reported that $I(CF_3)$ is 9.25 ± 0.04 eV. It appears that the difference between this value and the directly measured value is largely due to the fact that the adiabatic ionization potential of the radical is much lower than the vertical ionization potential, the configuration of the $CF_3^+$ ion being very different from that of the radical.

If we use the direct electron impact[9,10] value for $I(CF_3)$ in conjunction with our data for $A(CF_3^+)$ we find that $D(CF_3\text{–}COCF_3) \leqslant 4.16$ eV.

There are no other values reported for the $CF_3$–$COCF_3$ bond dissociation energy in hexafluoroacetone; because of the displacement reaction observed[13] when methyl radicals and hexafluoroacetone are present in the same system, it is likely[14] that the $CF_3$–$COCF_3$ bond is about 0.1 eV weaker than the corresponding bond in acetone (which has a strength of 3.8 eV), so that $D(CF_3\text{–}COCF_3) \sim 3.7$ eV.

Electron impact methods for measuring bond dissociation energies usually yield upper limit values because of the necessary neglect and uncertainty of the kinetic and excitation energies involved in the ionization and fragmentation processes. It may be therefore that our experimental value of $\leqslant 4.16$ eV compared with the estimated value of 3.7 eV reflects this uncertainty. However, the trifluoroacetyl radical has been shown to be unstable,[15] decomposing readily by reaction 3.

$$CF_3CO \longrightarrow CF_3 + CO \qquad (3)$$

Some or all of this energy difference of <0.46 eV may be used in decomposing the trifluoroacetyl radical formed in the initial ionization process; if this is so, then we may estimate a maximum value of 0.46 eV for the activation energy for reaction 3. Whittle,[16] using a kinetic method, has deduced an upper limit of 0.43 eV for this reaction.

Our data for $A(CF_3CO^+)$ should, in principle, provide an unequivocal value for $D(CF_3CO\text{–}CF_3)$, however no value is available for the ionization potential of the trifluoroacetyl radical. We may estimate $I(CF_3CO)$ if we assume that $D(CF_3CO\text{–}CF_3) = 3.7$ eV; our results indicate that $I(CF_3CO) < 8.3$ eV. This value may be compared with the value of 8.05 ± 0.17 eV reported[17] for $I(CH_3CO)$.

(*b*) *Negative Ion Formation. $O^-$ Ion Formation by Sulfur Dioxide.* The formation of negative ions by sulfur dioxide has been investigated by several workers and the appearance potential of the $O^-$ ion is sufficiently well established[4,5] at 4.2 eV to be used to calibrate the energy scale.

Our experimental data for this ion are shown in Figure 1; two resonance peaks are observed which have clear maxima but uncertain appearance potentials. Deconvolution of these data, using an electron energy distribution measured using $SF_6^-/SF_6$, give the results shown by the open circles. The threshold for the first peak is sharp and is separated from the peak maximum by 0.70 eV; this is in good agreement with the difference obtained by Kraus[4] (using a retarding-potential-difference technique) and by Dillard and Franklin.[5]

The onset of the second resonance peak is not quite resolved; Kraus[4] also was unable to completely separate the two peaks. The onset of the first peak and the minimum between the resonance peaks are separated by 2.4 eV in both our work and that of Kraus.

*Hexafluoroacetone* (HFA). In Table I we show the negative ion mass spectrum of HFA measured at nominal electron energies of 10 and 70 eV. The absence of ions such as $C^-$, $O^-$, and $C_2^-$ from the lower energy spectrum suggests that they are formed principally by ion-pair processes. We have studied the energy dependence of formation of the ions; $CF_3COCF_3^-$, $CF_3COCF_2^-$, $(CF_3)_2C^-$, $CF_3CO^-$, $CF_3^-$, $CF_2^-$, $CFO^-$, and $F^-$.

**Table I:** Negative Ion Mass Spectrum of Hexafluoroacetone at Electron Energies (Uncorrected) of 10 and 70 eV

| *m/e* | Ion | Rel. int., 10 eV | Rel. int., 70 eV |
|---|---|---|---|
| 12 | $C^-$ | 0 | 3.0 |
| 16 | $O^-$ | 0 | 21.5 |
| 19 | $F^-$ | 751 | 1000 |
| 24 | $C_2^-$ | 0 | 4.0 |
| 31 | $CF^-$ | 15.2 | 3.6 |
| 38 | $F_2^-$ | 0 | 3.0 |
| 43 | $C_2F^-$ | 0 | 2.0 |
| 47 | $CFO^-$ | 25.4 | 18.3 |
| 50 | $CF_2^-$ | 12.7 | 4.0 |
| 69 | $CF_3^-$ | 1000 | 257 |
| 97 | $CF_3CO^-$ | 10.1 | 17.0 |
| 147 | $CF_3COCF_2^-$ | 5.7 | 36.0 |
| 150 | $(CF_3)_2C^-$ | 7.6 | 4.0 |
| 166 | $CF_3COCF_3^-$ | 7.6 | 67 |

It is apparent from our data (discussed below) that several of the ions ($CF_3COCF_2^-$, $CF_3CO^-$, $CF_3^-$, $CFO^-$, and $F^-$) have almost identical appearance potentials (~3.1 ± 0.1 eV) and their respective resonance peaks attain a maximum value at ~4.2 ± 0.1 eV. This suggests a common origin for these ions and we suggest that this is an electronically excited unstable state of the ketone which subsequently decomposes to form the ions mentioned

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(13) R. M. Smith and J. G. Calvert, *J. Amer. Chem. Soc.*, **78**, 2345 (1956).

(14) S. W. Benson, private communication, 1969.

(15) P. B. Ayscough and E. W. R. Steacie, *Proc. Roy. Soc.*, **A234**, 476 (1956).

(16) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, **63**, 80 (1967).

(17) R. I. Reed and J. C. D. Brand, *ibid.*, **54**, 478 (1958).

$$CF_3COCF_3 + e \longrightarrow CF_3COCF_3^{-*} \longrightarrow$$

$$CF_3COCF_2^- + F \quad (4)$$

$$\longrightarrow CF_3CO^- + CF_3 \quad (5)$$

$$\longrightarrow CF_3^- + COCF_3(+CO + CF_3?) \quad (6)$$

$$\longrightarrow CFO^- + CF_2 + CF_3 \quad (7)$$

$$\longrightarrow F^- + CF_2COCF_3 \quad (8)$$

(*i*) *Charge-Transfer Reactions Involving the* $O^-$ *Ion.* The ionization curves for several of the ions (*e.g.*, $CF_3COCF_2^-$, $CF_3^-$, $F^-$) show inflections at energies ~5 eV; this corresponds to the resonance peak maximum observed for the $O^-$ ion formed by $SO_2$ (which was used to calibrate the electron energy scale). These inflections were not observed when $SO_2$ was not present in the ionization chamber; accordingly we attribute their occurrence to the charge-transfer reaction (9). This produces an unstable state of the parent ion which decomposes to yield the appropriate ions.

$$O^- + CF_3COCF_3 \longrightarrow O +$$

$$CF_3COCF_3^- \longrightarrow CF_3COCF_2^- \text{ etc.} \quad (9)$$

It is noteworthy that, even at the low ion source pressures maintained in this work, negative ion–molecule reactions may occur to a sufficient extent to contribute noticeably to the ionization efficiency curves.

(*ii*) $CF_3COCF_3^-$. The observation of a stable molecule–ion is relatively unusual; few other such ions have been observed. Its formation must involve the electron capture process

$$CF_3COCF_3 + e \longrightarrow CF_3COCF_3^- \quad (10)$$

Our data for this ion indicate two main regions of ion formation, one ~0 eV and the second[18] commencing at about 10 eV. In earlier work,[18] only the higher energy process was detected, the ion being formed as a result of secondary electron capture, the secondary electrons being produced by such positive ionization processes as $CF_3COCF_3 + e \rightarrow CF_3COCF_3^+ + 2e$.

At that time, we were unable to observe ion formation at very low electron energies; however, an improved experimental technique and introduction of a 3V dry cell into the electron energy circuit so that 'negative' voltages could be obtained has enabled us to examine the primary electron capture reaction.

When hexafluoroacetone was studied at electron energies ~0 eV, a parent ion was observed; admission of a small quantity of sulfur hexafluoride to the ionization chamber resulted in a considerable diminution of the $CF_3COCF_3^-$ ion intensity. This suggested that the electron attachment cross section for reaction 10 was much less than that for $SF_6^-$ ion formation by

$$SF_6 + e \longrightarrow SF_6^- \quad (11)$$

In Figure 2, we show the data obtained for $SF_6^-$ and $CF_3COCF_3^-$ ion formation as a function of the electron energy. A 50/50 mixture of hexafluoroacetone and sulphur hexafluoride was used; the two sets of ionization data have been normalized for convenience in presentation, the ordinate for $CF_3COCF_3^-$ being 58.9 times greater than that for $SF_6^-$.

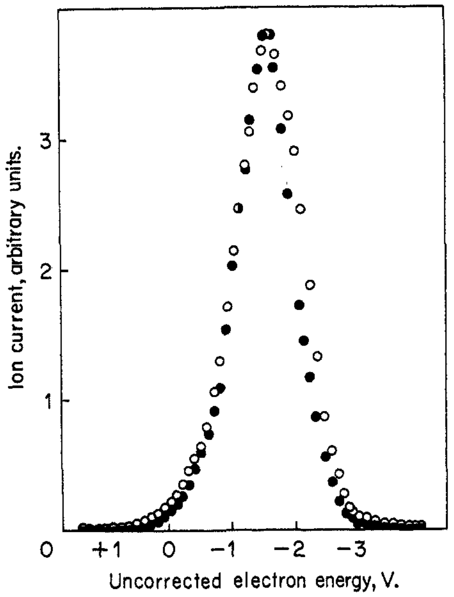

Figure 2. Ion current *vs.* electron accelerating energy. Full circles, $SF_6^-$; open circles, $CF_3COCF_3^-$. Ion current scale for hexafluoroacetone 58.9 times greater than that for $SF_6$.

Formation of the $SF_6^-$ ion in this energy region has been used to mirror the electron energy distribution and calibrate the electron energy scale.[7,8] It is apparent from Figure 2 that the $CF_3COCF_3^-$ and $SF_6^-$ ions have a very similar energy dependence, both ions attaining a maximum value at the same electron energy. The ionization curve for the ketone is slightly broader in the wings than is that for the hexafluoride, this may reflect either a slightly different energy dependence for electron attachment or the experimental uncertainties in measuring the very small ion currents for the $CF_3COCF_3^-$.

Because of their similar energy dependence we consider that the relative heights of the two ion peaks may be used to indicate the relative attachment cross-sections of reactions 10 and 11. If it is assumed that both ions have the same collection efficiency, then

$$\frac{\sigma_{SF_6}}{\sigma_{HFA}} = 58.9$$

where $\sigma_X$ refers to the electron attachment cross-section of X. A value of $3.6 \times 10^{-15}$ cm² has been reported[19] for $\sigma_{SF_6}$, so that $\sigma_{HFA} = 0.61 \times 10^{-16}$cm².

It has been observed that both sulfur hexafluoride[20]

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(18) J. C. J. Thynne, *Chem. Commun.*, 1075 (1968).

(19) R. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 4634 (1966).

(20) A. J. Ahearn and N. B. Hannay, *ibid.*, **21**, 119 (1953).

and hexafluoroacetone[18] form parent molecule-ions at higher electron energies as a result of secondary electron capture. We considered that competition between sulfur hexafluoride and hexafluoroacetone for secondary electrons might enable us to measure $\sigma_{SF_6}/\sigma_{HFA}$. Accordingly, using a 39.2:1 mixture of $CF_3COCF_3$: $SF_6$, we measured the intensities of the $CF_3COCF_3^-$ and $SF_6^-$ ions, $I_{HFA^-}$ and $I_{SF_6^-}$, at ten electron energy intervals over the range 15–60 eV. Our experimental data indicated that the ion current ratio, $I_{SF_6^-}/I_{HFA^-}$ was effectively constant over the entire energy range having a value of 1.44 ± 0.06; this result yields a value for $\sigma_{SF_6}/\sigma_{HFA}$ of 56 ± 2, which is in good accord with our directly-measured value at low electron energies.

An alternative explanation for the decrease in the $CF_3COCF_3^-$ ion current is the possibility of occurrence of the charge exchange reaction

$$CF_3COCF_3^- + SF_6 \longrightarrow CF_3COCF_3 + SF_6^- \quad (11a)$$

Our data for $SF_6^-$ formation cannot definitely distinguish between this reaction and reaction 11; however, at our ion source pressure ($\sim 5 \times 10^{-6}$ mm) although some collisions between $CF_3COCF_3^-$ and $SF_6$ will occur, we consider the probability of interactions occurring to a sufficient extent to account for the considerable decrease in $CF_3COCF_3^-$ ion current noted experimentally at very low $SF_6$ pressures ($\sim 10^{-7}$ mm) to be negligible unless the cross-section for reaction 11a is very large. The data obtained for secondary electron capture in the high energy study also suggest that reactions such as 11a may reasonably be neglected since, at these energies, other negative ion species (*e.g.*, $CF_3^-$, $CF_3CO^-$) will be present which might undergo charge transfer reactions.

$$X^- + SF_6 \longrightarrow SF_6^- + X$$

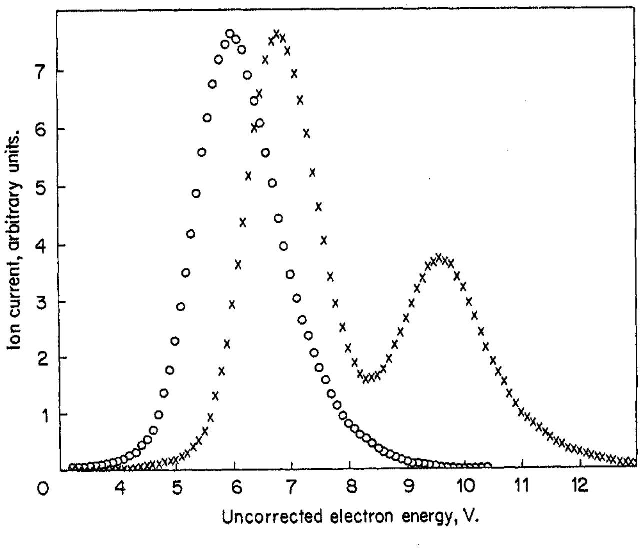

Figure 3. Ionization efficiency curve for $CF_3COCF_2^-/CF_3COCF_3$ (○) and $O^-/SO_2$ (×) ion formation.

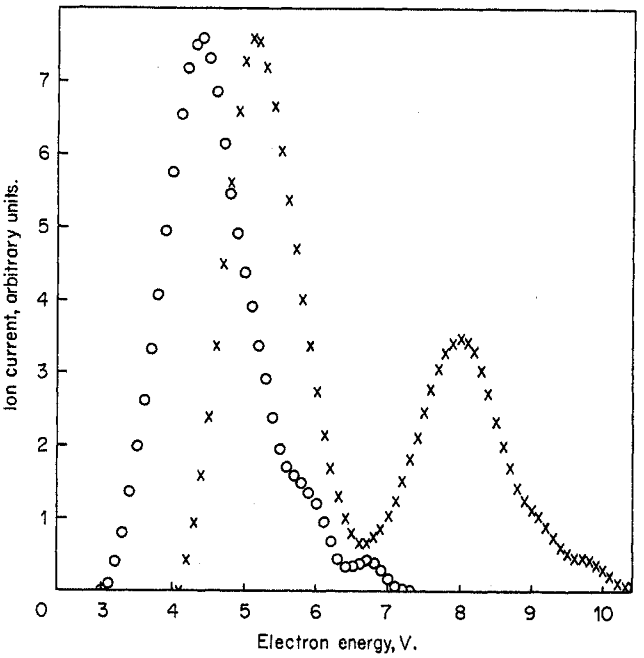

Figure 4. Deconvoluted results. $CF_3COCF_2^-/CF_3COCF_3$, ○; $O^-/SO_2$, ×.

If such reactions occurred significantly then it would result in the ratio $\sigma_{SF_6}/\sigma_{HFA}$ being greater at higher energies than at ~0 eV, whereas our experimental data show the two values to be in good agreement.

(*iii*) *$CF_3COCF_2^-$*. Typical experimental data and the smoothed, deconvoluted results are shown in Figures 3 and 4 together with the corresponding $O^-/SO_2$ ionization curves.

Examination of the pressure dependence of the $CF_3COCF_2^-$ ion current at low electron energies showed it to be a primary ion, we may therefore neglect the possibility of the ion being formed by secondary ionic reactions.

A sharp onset at 3.10 ± 0.10 eV is observed, the resonance peak reaching a maximum at 4.20 ± 0.05 eV; the peak width at half-height is 1.35 ± 0.05 eV. The common origin of the ions formed at this energy has been discussed above and we attribute $CF_3COCF_2^-$ ion formation to reaction 4.

If a value of ~5.2 eV is assumed for the bond dissociation energy $D(CF_3COCF_2\text{–}F)$, (values of 5.3, 5.2, and 5.0 eV having been reported for the C–F bond strengths in $CF_4$,[21] $C_2F_6$[22], and $C_6H_5F$[23], respectively), then using the relation: $D(CF_3COCF_2\text{–}F) \leqslant A(CF_3COCF_2^-) + E(CF_3COCF_2)$, a value of ~2.1 eV may be estimated for the electron affinity of the perfluoroacetonyl radical.

Figure 4 shows clearly the inflection in the ionization

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(21) C. R. Patrick, *Advan. Fluorine Chem.*, **2**, 18 (1961).

(22) K. A. G. MacNeil and J. C. J. Thynne, *Int. J. Mass Spectrom.*, **2**, 1 (1969).

(23) P. Smith, *J. Chem. Phys.*, **29**, 681 (1958).

**Table II:** Appearance Potentials (AP), Peak Maxima, and Peak Widths at Half Height (PW) of Negative Ions Formed by Hexafluoroacetone

| Ion | AP[a] | Max[a] | PW[a] | Process |
|---|---|---|---|---|
| $CF_3COCF_3^-$ | 0 | | | $CF_3COCF_3 + e \rightarrow CF_3COCF_3^-$ |
| $CF_3COCF_2^-$ | 3.10 ± 0.10 | 4.20 ± 0.05 | 1.35 ± 0.05 | $CF_3COCF_3 + e \rightarrow CF_3COCF_3^{-}\,*$<br>↓<br>$CF_3COCF_2^- + F$ |
| $(CF_3)_2C^-$ | 5.1 ± 0.1 | 6.4 ± 0.1 | 0.6 ± 0.1 | $CF_3COCF_3 + e \rightarrow (CF_3)_2C^- + 0$ |
| $CF_3CO^-$ | 3.10 ± 0.05 | 4.1 ± 0.1 | 1.0 ± 0.2 | $CF_3COCF_3^{-}\,* \rightarrow CF_3CO^- + CF_3$ |
| $CF_3^-$ | 3.0 ± 0.1 | 4.3 ± 0.1 | 1.5 ± 0.2 | $CF_3COCF_3^{-}\,* \rightarrow CF_3^- + CF_3CO$ |
| | 5.4 ± 0.1 | 6.7 ± 0.1 | 1.7 ± 0.1 | $CF_3COCF_3 + e \rightarrow CF_3^- + CO + CF_2 + F$ |
| | 8.2 ± 0.2 | 8.6 ± 0.1 | ... | ? |
| | 10.5 ± 0.2 | 11.0 ± 0.2 | ... | ? |
| $CF_2^-$ | 4.25 ± 0.10 | 5.25 ± 0.05 | 0.7 ± 0.1 | $CF_3COCF_3 + e \rightarrow CF_2^- + F + CO + CF_3$? |
| $CFO^-$ | 3.0 ± 0.1 | uncertain | 2 | $CF_3COCF_3^{-}\,* \rightarrow CFO^- + CF_2 + CF_3$ |
| | 5.3 ± 0.2 | 6.6 ± 0.1 | 2.0 ± 0.1 | $CF_3COCF_3 + e \rightarrow CFO^- + 2F + C_2F_3$ |
| $F^-$ | 3.1 ± 0.1 | 4.3 ± 0.2 | 1.3 ± 0.3 | $CF_3COCF_3^{-}\,* \rightarrow F^- + CF_2COCF_3$ |
| | 5.7 ± 0.1 | 7.2 ± 0.2 | 1.8 ± 0.3 | $CF_3COCF_3 + e \rightarrow F^- + CF_2 + CO + CF_3$ |
| | 9.0 ± 0.1 | ... | ... | $\rightarrow F^- + F + CO + 2CF_2$ |

[a] All values in eV.

curve which we have considered above to be the result of the charge-transfer reaction 9.

(*iv*) $(CF_3)_3C^-$. Our experimental data for this ion when smoothed and deconvoluted yield the values shown in Table II. Ion formation is attributed to the reaction

$$CF_3COCF_3 + e \longrightarrow (CF_3)_2C^- + O \qquad (12)$$

It is noteworthy that the resonance peak is very narrow, the width at half-height being only 0.6 eV. A value of ~0.6 eV may be estimated for the electron affinity of $(CF_3)_2C$ if the bond strength $D(O - C(CF_3)_2)$ is assumed to be similar to that in carbon dioxide, *i.e.*, ~5.7 eV.

(*v*) $CF_3CO^-$. At low electron energies, this ion is formed quite abundantly but not at 70 eV; this suggests that the ion-pair process $CF_3COCF_3 + e \rightarrow CF_3CO^- + CF_3^+ + 2e$ does not occur extensively. Our results for this ion are shown in Table II, and we consider reaction 5 to account for ion formation. If a value of 3.7 eV is assumed for $D(CF_3CO\text{-}CF_3)$, then our data yield a value of $\leqslant$ 0.6 eV for the electron affinity of the trifluoroacetyl radical.

(*vi*) $CF_3^-$. Ion formation in this case is rather complex; several appearance potentials are noted for this ion.

Initially ion formation occurred at 3.0 ± 0.1 eV and is attributed to decomposition of the electronically excited ketone by reaction 6. Because the trifluoroacetyl radical has been shown to have limited stability in the gas phase, the decomposition reaction 6 may involve the formation of CO and $CF_3$ as fragmentation products.

It is apparent from Figures 5 and 6 that the $CF_3^-$ ionization curve has inflections at ~5 eV and ~7.6 eV, *i.e.*, where the $O^-/SO_2$ ion reaches a maximum intensity; these inflections are attributed to the change transfer reaction mentioned above.

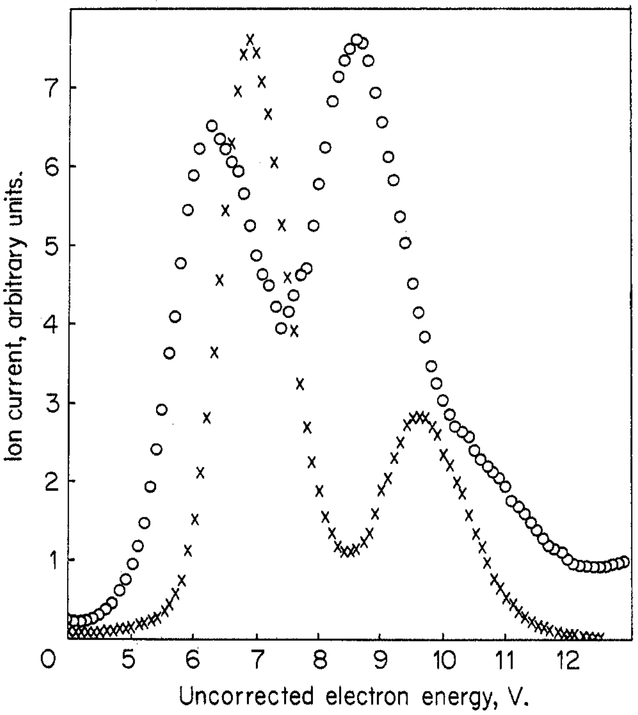

Figure 5. Ionization efficiency curve for $CF_3^-/CF_3COCF_3$, O, and $O^-/SO_2$, ×, ion formation.

A second resonance process is observed at 5.4 eV (based upon extrapolation of the upper part of the curve). If reaction 13 is responsible for ion formation at this energy, then our data yield a value of 2.5 eV for $E(CF_3)$; this may be compared with values of $\leqslant$2.6 eV[22] and 1.8 eV[24] reported for this quantity.

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(24) F. M. Page, private communication, 1968.

$$CF_3COCF_3 + e \longrightarrow CF_3^- + CO + CF_2 + F \quad (13)$$

Further resonance processes of very low cross section are noted at 8.2 and 10.5 eV; we cannot account for these ionization processes.

(*vii*) *$CF_2^-$*. Our data for this ion are shown in Table II; a narrow resonance peak having an onset at 4.25 ± 0.10 eV is obtained. If ion formation was due to the reaction

$$CF_3COCF_3 + e \longrightarrow CF_2^- + F + CO + CF_3 \quad (14)$$

then a value of $E(CF_2) \leqslant 3.75$ eV would be obtained; this seems improbably large. The narrow resonance peak would suggest that little excess energy was involved in the ionization process. A rearrangement reaction such as

$$CF_3COCF_3 + e \longrightarrow CF_2^- + CF_4 + CO \quad (15)$$

would yield a negative value for $E(CF_2)$; we are therefore unable to assign the ionization process responsible for $CF_2^-$ formation.

(*viii*) *$CFO^-$*. This ion must be formed as the result of rearrangement; ion formation is observed initially at 3.0 ± 0.1 eV and is attributed to reaction 7. Although a sharp onset is obtained at this energy, the resonance peak is broad (~2 eV) and does not attain a clear maximum before a second resonance process occurs at 5.3 eV. This resonance peak is also broad and this perhaps suggests the involvement of considerable excess energy in the rearrangement.

$$CF_3COCF_3 + e \longrightarrow CFO^- + 2F + C_2F_3 \quad (16)$$

The second ionization process may correspond to reaction 16, *i.e.*, the C–O bond is broken and the oxygen transferred to a CF group in the rearrangement. This probably would have higher energy requirements than reaction 7 where simple fluorine transfer to CO may be involved but such assignments are tentative.

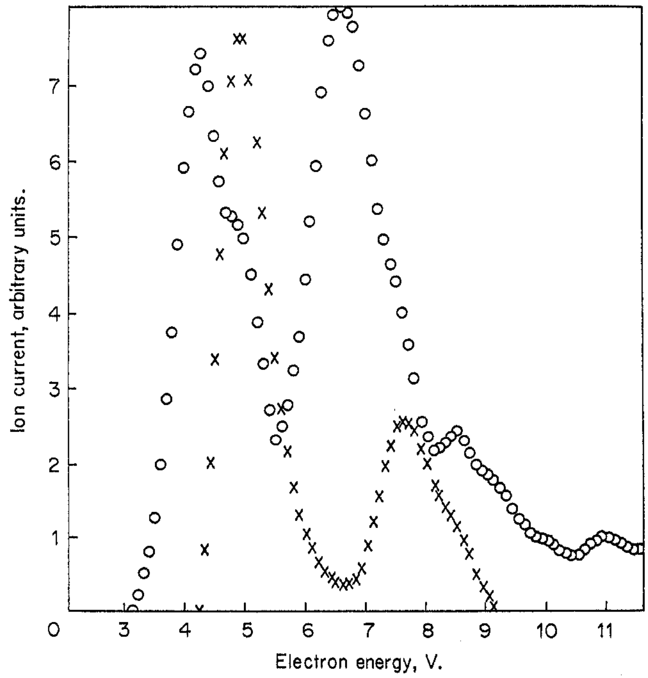

Figure 6. Deconvoluted results. $CF_3^-/CF_3COCF_3$, O; $O^-/SO_2$, X.

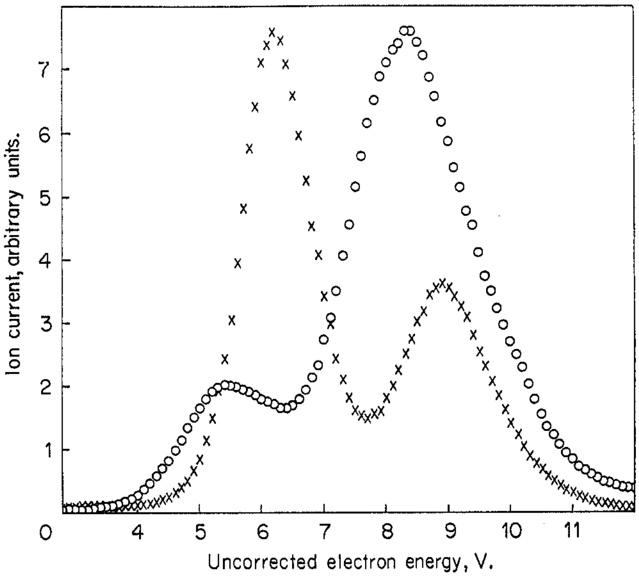

Figure 7. Ionization efficiency curve for $F^-/CF_3COCF_3$, O and $O^-/SO_2$, X, ion formation.

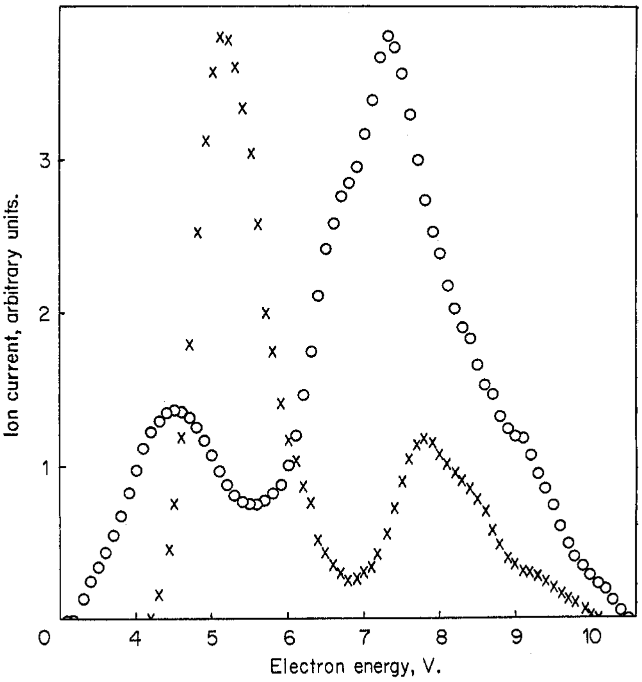

Figure 8. Deconvoluted results. $F^-/CF_3COCF_3$, O; $O^-/SO_2$, X.

The heat of formation of the fluoroformyl radical, $\Delta H_f(CFO)$, has been estimated[3] to be −1.7 eV, so that our data for reaction 7 indicate $E(CFO)$ ~3.3 eV. A study[3] of $CFO^-$ ion formation by carbonyl fluoride showed $E(CFO) = 2.7$ eV; the resonance peak in that work was much narrower than that found in this study (~0.5 eV compared with ~2.0 eV), which may reflect the excess energy involved in the hexafluoroacetone rearrangement.

(*ix*) *F*$^-$. Our results for this ion are summarized in Table II and typical data shown in Figures 7 and 8.

Inflections in the deconvoluted curve at ~5 and ~7.5 eV we attribute to the charge-transfer reaction involving the O$^-$ ion. The first appearance potential at 3.1 ± 0.1 eV is considered to be the result of reaction 8 discussed previously; a second process of much larger cross section occurs at 5.7 ± 0.1 eV. If reaction 17 is responsible for the increase in the ion current at this energy, then a maximum value of 2.6 eV may be deduced for the bond dissociation energy $D(CF_2\text{–}COCF_3)$ if we assume that $D(CO\text{–}CF_3) = 0$ eV.

$$CF_3COCF_3 + e \longrightarrow F^- + CF_2 + CO + CF_3 \quad (17)$$

A further ionization process of very low cross-section may be seen on the tail of the second resonance peak, the onset energy being 9.0 eV.

$$CF_3COCF_3 + e \longrightarrow F^- + F + CO + 2CF_2 \quad (18)$$

The minimum enthalpy requirement for reaction 18 is 9.0 eV and we therefore attribute ionization to this reaction.

(*c*) *Thermochemical Data.* The following values for the heats of formation have been used in this work (in eV) $CF_3COCF_3$ −15.1; $CF_3$−5.2;[25] $CF_2$−1.6;[26] CF, 3.2;[27] F, 0.8;[27] CO, −1.1;[27] and $CF_3^+$, 3.7.[28]

The heat of formation of hexafluoroacetone has been estimated using the additivity rules[29] based upon the C–C and C–F bond contributions to the enthalpies of various fluorine-containing molecules.[21,29]

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# Rate Constants and Transient Spectra in the Gas-Phase Reactions of Hydrogen Atoms. Substituents Effects in Monosubstituted Benzenes[1]

**by Myran C. Sauer, Jr.,[2] and Inder Mani**

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Transient spectra and rate constants have been obtained, using the pulse-radiolysis technique, for the gas phase reactions of hydrogen atoms with a series of monosubstituted benzenes, naphthalene, the xylenes and pyridine. Arrhenius parameters have been determined for most of these compounds by varying the temperature within the range 25–120°. The rate constants for $H + C_6H_5X$ can be correlated with the Hammett $\sigma$ values of the substituents, X, and the nature of the correlation indicates that the hydrogen atom is electrophilic in these reactions.

## Introduction

The transient spectra and rate constants have previously been measured in the case of hydrogen atom addition to benzene and toluene in the gas phase, and the technique of making such measurements has been described. That hydrogen atoms are produced during the pulse (microsecond) of electrons and subsequently react in a pseudo-first-order manner with the organic compound has been shown.[3] We have now made similar measurements for a series of monosubstituted benzenes in order to determine the relationship between the observed rate constants and the Hammett $\sigma$-values of the substituent groups.

## Experimental Section

A complete description of the basic apparatus used in this pulse-radiolysis study has been given pre-

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(1) Work performed under the auspices of the United States Atomic Energy Commission.

(2) To whom requests for reprints should be sent.

(3) M. C. Sauer, Jr., and B. Ward, *J. Phys. Chem.*, **71**, 3971 (1967).