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Molecular Dissociation by Electron Bombardment: A Study of $SiCl_4$*

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The first part of this paper deals with molecular dissociation in general, with reference to the determination of appearance potentials of molecular fragments. Appearance potentials are generally determined from plots of ion current *versus* electron energy by either of two methods: determination of the energy at which ion current is first detected; or location of the intercept with the energy axis of the extrapolation of the straight line portion of the ionization efficiency curve. It is pointed out that the first procedure has a rather indefinite relation to the physical quantities involved and that the value obtained by the second method corresponds quite closely to the energy necessary to produce a transition through the center of the Franck-Condon region. The last section of the paper contains an analysis of data obtained in a study of the dissociation of silicon tetrachloride. Both positive and negative ions are formed in processes resulting in most of the possible configurations. The data are correlated with values of dissociation energies from external data, and estimates are made of the ionization energies of the radicals involved. Ionization energies of $SiCl_4$ and $SiCl_2$ are measured directly and are found to be 11.6±0.2 volts and 11.8±0.3 volts, respectively.

INTRODUCTION

THE use of a mass spectrometer to determine the energy necessary to produce a particular type of molecular dissociation is quite common.[1] This energy, generally called the appearance potential of the ions observed, is composed of three quantities: the dissociation energy necessary to disrupt the molecule into various fragments; an ionization energy (or electron affinity) necessary to produce an ion from one of the dissociated fragments; and excess energy resulting from the dissociation process which may be manifest either as excitation energy of the fragments or as kinetic energy of relative motion of the dissociation products.

This latter quantity is not of great interest *per se* but it is desirable to know it in order that the dissociation energies and ionization energies may be determined. It has only been determined for a few simple processes[2] and is generally found to be quite small, around one volt or less, for energies which are just sufficient to produce the dissociation. The procedure is to measure directly, by stopping potentials, the kinetic energy of dissociation as a function of bombarding energy, the difference between these two quantities giving the difference of potential energy of the molecule in its initial and final states. The recently developed use of retarding fields on analyzed ion beams[3] will make it possible to perform these measurements for any dissociation process, the advantage of this method over that of Lozier being that each type of ion may be studied separately and identified by its e/m value. This should also provide information about the shapes of surfaces representing the potential energy of various configurations of the molecule.

Of the other two quantities, a knowledge of one permits a limit to be placed on the other, the uncertainty being caused by the unknown excess energy. For silicon tetrachloride neither the dissociation energies nor the ionization energies are known accurately beforehand. However, most molecular configurations are involved in production of both positive and negative ions

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[1] A list of the most recent references for substances that have been studied is given by J. A. Hipple, J. App. Phys. **13**, 551 (1942).

[2] J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932); W. W. Lozier, Phys. Rev. **46**, 268 (1934).

[3] J. A. Hipple, R. E. Fox, and E. U. Condon, Phys. Rev. **69**, 347 (1946).

so that two checks are obtained on each dissociation energy, and the processes resulting in negative chlorine ions involve the electron affinity of chlorine which is fairly well known.

APPEARANCE POTENTIAL DETERMINATION

There is always some question as to just how curves of ion current *versus* electron energy should be interpreted for determining appearance potentials. The energy at which ion current is "first detected" is one definition of appearance potential often used, while the other method is to extrapolate the straight line portion of the ionization efficiency curve back to zero current and take the intercept with the voltage axis as the appearance potential. The principle objection raised to the first method is that the electrons in the ionizing beam have a definite spread in energy caused by the high temperature of the source and perhaps also caused by the fact that the source is not an equipotential surface. This difficulty can be overcome by calibrating all measurements against some standard whose ionization energy is well known, provided the true ionization efficiency curves of the standard and unknown processes do not differ appreciably near their origins. The objection to the second method is that it assumes that the ionization efficiency is a linear function of the energy at the onset of the curve.[4] The discussion to follow shows that in dissociation processes releasing kinetic energy the two methods would be expected to give significantly different values. This effect is independent of any of the objections to either method of analysis mentioned above, and would result in a "tail" at the base of the ionization efficiency curve for any ion that acquires kinetic energy in the dissociation process. Neither method is correct or wrong, but each has a different meaning in terms of the physical ideas used in explaining molecular dissociation.

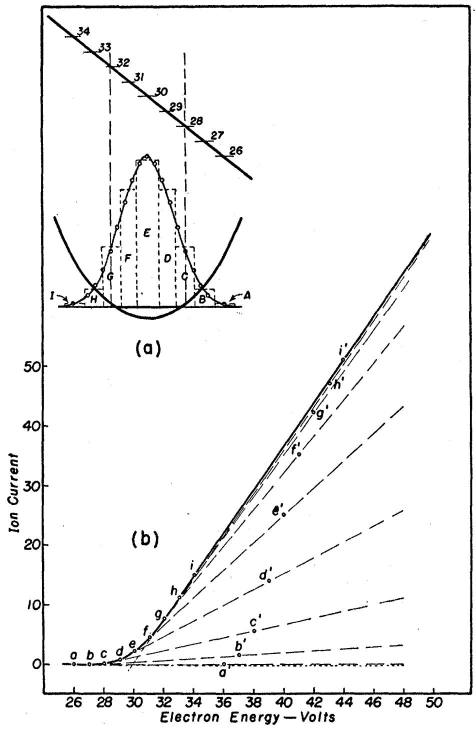

FIG. 1. Construction to explain shape of appearance potential curve. (See text.)

In Fig. 1a are shown schematic sections of the potential energy curves for the hydrogen molecule. The lower curve is for the normal state while the line across the top is a straight line approximation of the curve for the repulsive state of the molecular ion, the numbers indicating the potential energy in electron volts. Superimposed on the lower curve is the expectation function of the lowest vibrational state, while the dashed vertical lines represent the limits of nuclear oscillations if the molecule be considered a classical harmonic oscillator; that is, they define the Franck-Condon region. This curve may be interpreted as indicating the relative number of molecules in a gas having a given nuclear separation. Thus a beam of electrons of say 28 volts would be able to excite to the repulsive H_2^+ state only that fraction of the molecules represented by the area under the expectation function to the right of the Franck-Condon limit. As the energy is increased a larger fraction of the molecules will become susceptible for excitation until at about 34 volts, essentially all of the molecules may be excited to the upper state. Hence, if it be assumed, as is customary, that the probability of the transition is proportional to the excess energy above the minimum required energy, it is evident that the ion current would increase more rapidly than linearly in the energy range from 26 to 34 volts

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[4] D. P. Stevenson and J. A. Hipple, Phys. Rev. 62, 237 (1942).

since more molecules are constantly being made available for excitation. Because the probability of finding a nuclear separation outside of the limits given by the Franck-Condon region is very small, the curvature of the ionization efficiency curve will be noticeable only in the range from 28 to 32 volts.

The shape of the ionization efficiency curve may be approximated graphically for this simplified case and is shown in Fig. 1b. The area under the expectation curve is divided into sections A, B, C, $\cdots$, representing those fractions of molecules which can undergo transitions when supplied with energies of 26, 27, 28, $\cdots$ volts. The contributions to the ion current from each of these sections is then given by the dashed lines aa', bb', cc', $\cdots$, of Fig. 1b. These are drawn on the assumption that the transition probability increases linearly with surplus energy above the minimum energy required for the process by making the ion currents at energies of $26+10$, $27+10$, $\cdots$ proportional to the areas A, B, $\cdots$ and connecting the points a and a', b and b' $\cdots$ with straight lines. The curve thus obtained, $abc\cdots ii'$, represents the ion current as a function of bombarding electron energy.

When the straight line portion of the curve is now extrapolated back to zero current, the intercept on the energy axis is 30 volts. This is just the energy necessary to produce a transition between the two states if the molecule has the equilibrium nuclear separation; that is, the transition is through the center of the Franck-Condon region. The energy range over which a distinct curvature is evident will also give a rough idea of the energies at which the upper potential energy curve crosses the Franck-Condon region.

Several factors will determine the exact shape of the ionization efficiency curve. In the case above, the expectation function for the lowest vibration state was used, but any expectation function which is symmetrical about the equilibrium position could have been used and the extrapolated appearance potential would have been the same. A symmetrical energy distribution of ionizing electrons would spread the curve slightly but would still give a straight line extrapolation corresponding to a transition through the center of the Franck-Condon region. Since the actual distribution is Maxwellian, which gives more electrons with energy greater than the most probable energy, the appearance potential determined by this method would be slightly lower than for a symmetrical distribution.

The factor that affects the ionization efficiency curve most strongly, and about which least is known, is the potential energy curve for the state to which the transition occurs. The majority of known curves have minima at larger nuclear separations than for the normal state, and in the Franck-Condon region they are slightly concave towards smaller separations. The result of this slight concavity would be to give a higher extrapolated appearance potential than is obtained with a straight line approximation. However, this effect is very slight if the concavity is not great and is partly compensated by the opposite effect resulting from a Maxwellian distribution of the electrons.

In cases of molecular dissociation and ionization, then, the two methods of determining appearance potentials have quite different physical interpretations. The electron energy at which current is "first detected" in Fig. 1a would evidently cause excitation of molecules with nuclear separations greater than the classical limit; just what point it corresponds to will depend on the distribution in energy of the ionizing electrons, the sensitivity of the amplifier, the probability of the process being studied and the angle at which the upper potential energy curve intersects the Franck-Condon region. The straight line extrapolation method, however, gives the energy necessary to produce a transition through the center of the Franck-Condon region subject to the conditions outlined above. Neither method, in general, gives the true dissociation energy, or dissociation plus ionization energy, so that an independent study of the kinetic energy of dissociation products as a function of bombarding energy would be necessary to determine this quantity. This report will use the straight line extrapolation method. Although the above arguments were given for a simple diatomic molecule, it is evident that similar considerations would hold in the more complicated dissociation processes in polyatomic molecules.

Production of negative ions by resonance capture of an electron gives appearance potential curves with much sharper breaks than for positive ions, so that the effect of a spread of the electron energies would be quite different in the two cases. In fact, some resonance curves for negative ions have a width that is quite comparable with the energy distribution of the electrons which is quite broad in the experiments to be described because of the high temperature of the tungsten filament and the fact that it is not an equipotential surface. In these cases an error nearly as large as half the width of the energy distribution could conceivably occur by using the method of first detected current. To determine the value analogous to that obtained with the extrapolation method, the appearance potential is taken as the energy at the maximum of the resonance peak.

EXPERIMENTAL

The mass spectrometer used for this work was a Nier type 60° instrument which has been described in some detail in a previous paper.[5] Principle changes from Nier's published design are the use of a permanent magnet for the deflecting field, and the use of an electromagnet on the ion source. The electromagnet was placed on the ion source to increase the ion current and resolving power but it is also necessary in appearance potential measurements to keep the energy of the ionizing electrons at a known value. Since the electrons are subjected to the ion draw-out potential of about 3 volts after passing into the ionizing region their energy on collision could be appreciably different from the measured value. However a magnetic field of a hundred gauss is sufficient to keep the energy constant within a few percent for initial energies as low as 1 volt. The electron energy scale was calibrated by introducing argon into the instrument with the gas to be studied.

The silicon tetrachloride used for the analyses was kindly supplied by C. M. Olson, Pigments Department, E. I. du Pont de Nemours and Company. It had not been subjected to the pyralysis treatment used to "crack" out impurities of carbon tetrachloride but a previous

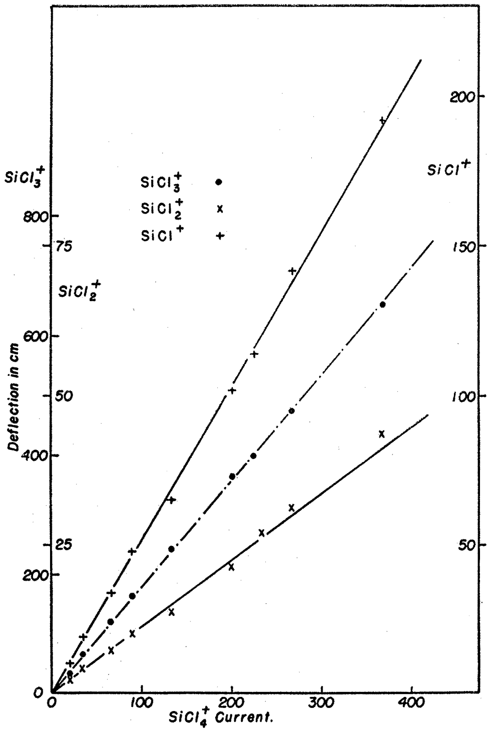

FIG. 2. Ion current for fragment ions *vs.* ion current for parent ion at different pressures.

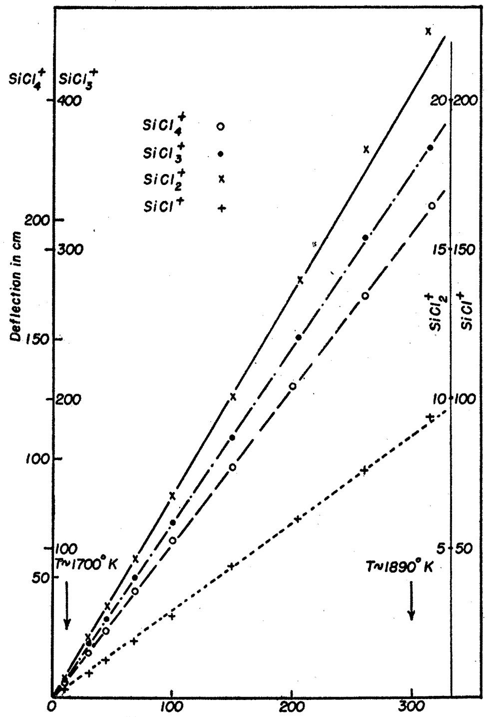

FIG. 3. Ion current *vs.* ionizing current.

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[5] J. E. Taylor, Rev. Sci. Inst. 15, 1 (1944).

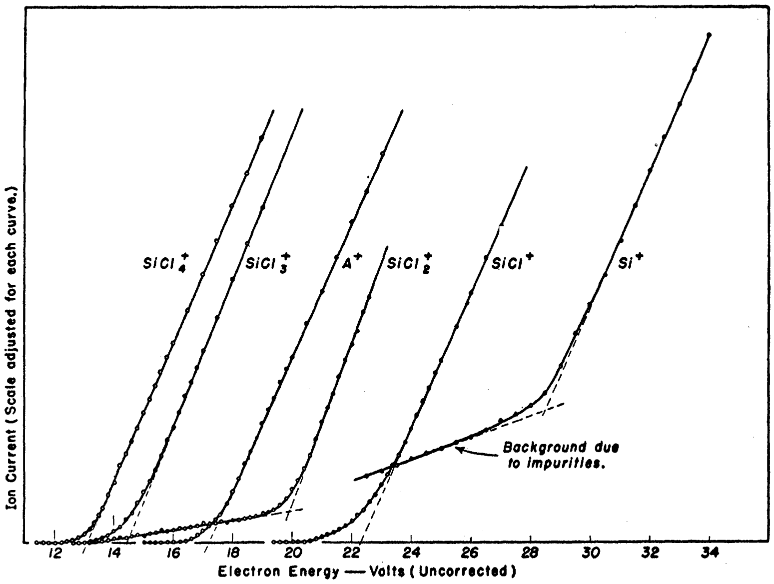

FIG. 4. Appearance potential curves for singly-charged positive ions in $SiCl_4$.

investigation showed that such impurities were present to less than 0.1 percent.[6] Before admitting the gas to the system for analysis the pressure in the ion source was about 10^{-6} mm of Hg, the impurities being water and some carbon monoxide and nitrogen. While taking measurements the pressure in the ion source was kept between 10^{-4} and 10^{-5} mm of Hg. Once $SiCl_4$ had been admitted to the system a disturbing background of HCl appeared, probably caused by the reaction $SiCl_4+2H_2O \rightarrow 4HCl+SiO_2$. This could not be pumped out and the Cl^+ ions from dissociation of HCl make the appearance potential curve for Cl^+ from $SiCl_4$ invalid.

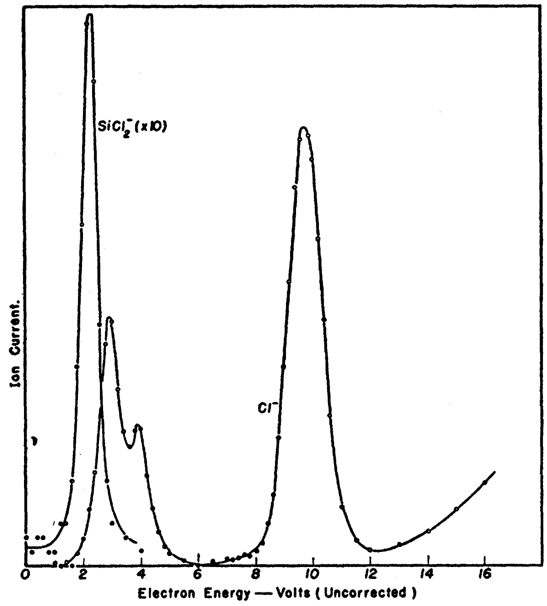

FIG. 5. Appearance potential curves for negative ions in $SiCl_4$.

The mass spectrometer used does not employ differential pumping on the ion source, so measurements of ion current as a function of pressure and filament temperature were made to distinguish processes due to electron bombardment of $SiCl_4$ from possible secondary processes. Figure 2 shows various ion currents plotted against $SiCl_4^+$ current. (This current is a more accurate pressure indicator than the ionization gauge.) The filament temperature and ionizing current could not be varied independently so in Fig. 3 are shown the ion currents plotted as a function of total filament emission, the filament temperature varying by about 190°C in this range. It is seen that with the exception of $SiCl_2^+$ the currents are linear functions of the variables and hence caused by primary processes. The fact that the $SiCl_2^+$ current increases more rapidly at high pressure, and especially at high temperature, indicates that $SiCl_2$ due to thermal decomposition is probably present. This is also indi-

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[6] R. H. Vought, Report No. 588 for OSRD Contract OEMsr-388, Division 14, NDRC, October 5, 1945.

Table I. Ions formed in $SiCl_4$.

Ion	Relative intensity at 75 v	Appearance potential (volts)	Suggested process $SiCl_4\rightarrow$:	Minimum energy required (volts)	Excess energy or ionization potential deduced (volts)
$SiCl_4^+$	56	11.6 ± 0.2	$SiCl_4^+$	$I(SiCl_4)$	$I(SiCl_4)=11.6$
$SiCl_3^+$	100	12.9 ± 0.2	$SiCl_3^++Cl$	$4.4+I(SiCl_3)$	$I(SiCl_3)\leqslant 8.5$
			$SiCl_3^++Cl^-$	$0.6+I(SiCl_3)$	$I(SiCl_3)\leqslant 12.3$
$SiCl_2^+$	4.1	11.8 ± 0.3	$SiCl_2\rightarrow SiCl_2^+$	$I(SiCl_2)$	$I(SiCl_2)=11.8$
		18.4 ± 0.3	$SiCl_2^++Cl_2$	15.2	$T+E=3.2$
			$SiCl_2^++2Cl$	17.7	$T+E=0.7$
$SiCl^+$	13	20.5 ± 0.3	$SiCl^++Cl_2+Cl$	$8.1+I(SiCl)$	$I(SiCl)\leqslant 12.4$
			$SiCl^++3Cl$	$10.6+I(SiCl)$	$I(SiCl)\leqslant 9.9$
Cl^+	5.5				
Si^+	14	27 ± 1	Si^++2Cl_2	18.0	$T+E=9.0$
			Si^++Cl_2+2Cl	20.4	$T+E=6.6$
			Si^++4Cl	22.9	$T+E=4.1$
$SiCl_2^-$	0.25	0.8 ± 0.3	$SiCl_2^-+Cl_2$	5.9	$EA(SiCl_2)\geqslant 5.1$
			$SiCl_2^-+2Cl$	3.4	$EA(SiCl_2)\geqslant 2.6$
			$SiCl_2\rightarrow SiCl_2^-$		
Cl^-	4.0	1.4 ± 0.3	Cl^-+SiCl_3	0.6	$T+E=0.8$
		2.4 ± 0.3	Cl^-+SiCl_2+Cl	2.1	$T+E=0.3$
		8.2 ± 0.3	$Cl^-+SiCl+Cl_2$	4.3	$T+E=3.9$
			$Cl^-+SiCl+2Cl$	6.8	$T+E=1.4$
$SiCl_3^{++}$	4.9	33.8 ± 0.5			
$SiCl_2^{++}$	0.65	37.3 ± 0.5			
$SiCl^{++}$	1.2	42 ± 1			

cated by the fact that while pumping out the system a background current of $SiCl_2^+$ ions greater than that owing to $SiCl_3^+$ ions was observed, whereas the ratio while admitting gas was 25 to 1 with the $SiCl_3^+$ current larger.

RESULTS

The ion currents due to the various ions observed in silicon tetrachloride are shown in Figs. 4 and 5. The appearance potentials from these curves and the relative abundances of each type of ion are recorded in Table I. This also includes the results of some energy calculations to be discussed later. The relative intensity of each ion was determined from a measurement of the current due to one isotope and then dividing by the fraction of the total number of ions of this type having this mass, as determined from the relative abundances of the isotopes of silicon and chlorine. Corrections were made for Cl^+ and Si^+ currents due to impurities and for Cl^- and $SiCl_2^-$ currents due to the poor negative ion collecting efficiency of the mass spectrometer. The efficiency was known to be low from a comparison of measurements made on carbon tetrachloride with the results of Baker and Tate.[7] It was also found that above 15 volts the ionization efficiency curves for negative ions had shapes characteristic of the instrument rather than of the gas, so that appearance potential measurements of negative ions from ion pair production were invalid. The only explanation suggested for this low efficiency is improper geometry of the slit system, as evidenced by extreme sensitivity of ion current to position of the ion source electromagnet.

DISCUSSION

The notation to be used is: $A(X^+)$—appearance potential of X^+; $D(XY)$—heat of dissociation of XY; $I(X)$—ionization energy of X; $EA(X)$—electron affinity of X; $T+E$—excess energy in

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[7] R. F. Baker and J. T. Tate, Phys. Rev. **53**, 683A (1938).

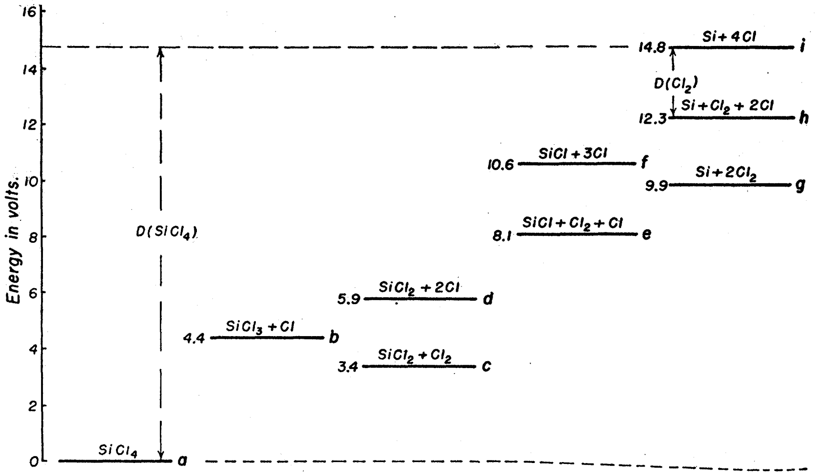

FIG. 6. Energies of the possible configurations of one silicon and four chlorine atoms relative to that of the parent molecule, $SiCl_4$.

a dissociation process, where T represents kinetic energy of relative motion and E is the excitation energy of the dissociation products.

For relating the observed quantities to other properties of the gas the following estimates of heats of dissociation of $SiCl_4$ can be made. From the usual Born cycle the heat of dissociation of $SiCl_4$ is

$$D(\mathrm{SiCl_4}) = Q(\mathrm{SiCl_4}) + 2D(\mathrm{Cl_2}) + L(\mathrm{Si}),$$

where $Q(\mathrm{SiCl_4})$ is the heat of formation of $SiCl_4$ and $L(\mathrm{Si})$ is the heat of sublimation of silicon. Using values from Bichowsky and Rossini[8] $D(\mathrm{SiCl_4}) = 142.5 + 2\times 56.9 + 85 = 341$ kilocalories per mole, or 14.8 electron volts. This determines the separation of levels *a* and *i*, Fig. 6. Evidently, level *h* is below *i* by $D(\mathrm{Cl_2}) = 2.47$ volts, and *g*, *e*, and *c* are below *h*, *f* and *d* by the same amount. $D(\mathrm{SiCl})$ was determined[9] as 4.2 volts from the vibrational constants for transitions to the six lowest levels of the ground electronic state from the data of Jevons.[10] Parti and Samuel[11] estimate $D(\mathrm{SiCl_2})$ as $\frac{3}{5}D(\mathrm{SiCl_4})$. This relation holds for the tin chlorides and gave consistent results when applied to other halogen compounds of this type. $D(\mathrm{SiCl_3})$ may be estimated from the $\mathrm{Si}^{IV}-\mathrm{Cl}$ bond energy. Asundi, Karim, and Samuel[12] point out that this is not simply $\frac{1}{4}D(\mathrm{SiCl_4})$ since the electronic configuration of silicon in the $SiCl_4$ molecule is sp^3 rather than s^2p^2 of the normal atom. Using their estimate of this excitation energy the strength of the $\mathrm{Si}^{IV}-\mathrm{Cl}$ bond is determined as $\frac{1}{4}(14.8+2.7) = 4.4$ volts.

Since the electron affinity of chlorine is known to be 3.8 volts,[13] calculations on processes involving this ion will give closer checks on heats of dissociation than can be obtained with processes involving positive ions such as $SiCl_3^+$ for which ionization energies are not known. The first two resonance appearance potentials for Cl^- must evidently correspond to dissociation to levels *b* and *d*, Fig. 6. The excess energy in each process is the difference between the appearance potential and the algebraic sum of the dissociation energy and electron affinity. Thus we have $T+E = 1.4-(4.4-3.8) = 0.8$ volt for the process giving $SiCl_3 + Cl^-$, and $T+E = 2.4-(5.9-3.8) = 0.3$ volt for the process $SiCl_4 \rightarrow SiCl_2 + Cl + Cl^-$. The energies required to produce Cl^- by transitions to *e*, *f* and *h* are 4.3, 6.8 and 8.5 volts, respectively. The 8.2 volts for the third appearance potential for Cl^- is not sufficient for the latter transition and would leave an unlikely large amount of excess energy for the former, so that the process is probably $SiCl_4 \rightarrow SiCl + 2Cl + Cl^-$ requiring 6.8 volts and leaving 1.4 volts excess energy. This may still be some-

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[8] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

[9] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

[10] W. Jevons, Proc. Roy. Soc. London **48**, 563 (1936).

[11] Y. P. Parti and R. Samuel, Proc. Phys. Soc. London **49**, 568 (1937).

[12] R. K. Asundi, M. Karim, and R. Samuel, Proc. Phys. Soc. London **50**, 581 (1938).

[13] H. S. W. Massey, *Negative Ions* (Cambridge University Press, London, 1938).

what large and might indicate that the long extrapolation used to get $D(\mathrm{SiCl})$ is inaccurate. However, the width of this resonance peak is seen to be about a volt greater than the maximum possible spread in energy of the electrons,* indicating that the potential energy surface for the system $\mathrm{SiCl-Cl-Cl-Cl^-}$ intersects the Franck-Condon region over a range of at least a volt and it may well be above the asymptote for infinite separation by about a volt.

If the $\mathrm{SiCl_2^-}$ ions appearing at 0.8 volt are produced from $\mathrm{SiCl_4}$ the electron affinity must be at least equal to the energy required for a transition to levels c or d, minus $A(\mathrm{SiCl_2^-})$. Thus $EA(\mathrm{SiCl_2}) \geq 2.6$ or 5.1 volts. Either value seems large never to have been reported and is larger than would be expected for such a molecule. Because of the non-linearity of $\mathrm{SiCl_2^+}$ current with temperature and pressure, and because of the type of appearance potential curve found for $\mathrm{SiCl_2^+}$ ions, free $\mathrm{SiCl_2}$ molecules were probably present in the ion source and the ions observed here could be produced by simple capture of an electron. If this is the case nothing can be said of the electron affinity of $\mathrm{SiCl_2}$ except that it exists.

Of the processes leading to formation of positive ions the simplest is ionization of the parent molecule and this requires no discussion. The process resulting in $\mathrm{SiCl_3^+}$ ions is not so easily identified since it could be accompanied by either a free or negatively ionized chlorine atom. The energies required would differ by $EA(\mathrm{Cl})$, and the ionization energy for $\mathrm{SiCl_3}$ deduced from the two cases is ≤ 8.5 volts or ≤ 12.3 volts. Using the interpretation presented in the first part of this paper, the foot of the ionization efficiency curve for $\mathrm{SiCl_3^+}$ indicates that about one volt of kinetic energy is released on dissociation, so that the first possibility would give too low a value for $I(\mathrm{SiCl_3})$. For this reason, and because $\mathrm{Cl^-}$ ions from ion pair production are also observed at about 13 volts, the process is probably $\mathrm{SiCl_4 \rightarrow SiCl_3^+ + Cl^-}$. Using the comparison with Baker and Tate's work on carbon tetrachloride[7] to determine the negative ion collecting efficiency of this mass spectrometer, the corrected value for $\mathrm{Cl^-}$ current is still much smaller than the $\mathrm{SiCl_3^+}$ current, so that $\mathrm{SiCl_3^+ + Cl}$ should also be produced at 3.8 volts higher energy than the 12.9 volts attributed to the process $\mathrm{SiCl_4 \rightarrow SiCl_3^+ + Cl^-}$. However no break in the ionization efficiency curve is observed. It is possible that the estimate of efficiency is wrong and that equal numbers of $\mathrm{SiCl_3^+}$ and $\mathrm{Cl^-}$ ions are produced. The uncertainty here must be attributed to the poor negative ion collecting efficiency.

Two appearance potentials are found for $\mathrm{SiCl_2^+}$. From the previous evidence for the existence of free $\mathrm{SiCl_2}$ in the ion source the 11.8-volt value is attributed to the ionization potential of $\mathrm{SiCl_2}$. The second value at 18.4 volts may then be assigned to the process $\mathrm{SiCl_4 \rightarrow SiCl_2^+ + 2Cl}$, which should require 17.7 volts energy. This leaves the reasonable value of 0.7 volt for excess energy.* That the curve for $\mathrm{SiCl_2^+}$ ions shown in Fig. 4 is actually owing to $\mathrm{SiCl_2^+}$ and not an impurity was demonstrated by taking measurements on the isotopes $\mathrm{Si^{28}Cl^{35}Cl^{37}}$ and $\mathrm{Si^{28}Cl^{35}Cl^{35}}$. Identical curves were obtained in both cases.

If the 20.5-volt appearance potential for $\mathrm{SiCl^+}$ be attributed to production of $\mathrm{SiCl^+ + 3Cl}$, a limit on the value of $I(\mathrm{SiCl})$ is determined as $I(\mathrm{SiCl}) \leq 20.5 - 10.6 = 9.9$ volts. From the appearance potential curve it is seen that there is probably some kinetic energy released by the process so this may make the value seem low. However, it is not unreasonably low, since SiCl is a highly polymeric substance[14] and this tendency to bond formation indicates that a relatively free electron is present. The alternative explanation that the products are $\mathrm{SiCl^+ + Cl_2 + Cl}$, would be the only case observed in which two chlorine atoms came off as a molecule rather than as free atoms.

The production of $\mathrm{Si^+}$ ions at 27 volts is probably due to the process $\mathrm{SiCl_4 \rightarrow Si^+ + 4Cl}$, which requires an energy of $D(\mathrm{SiCl_4}) + I(\mathrm{Si})$. $I(\mathrm{Si})$ being 8.14 volts,[8] this value is 22.9 volts. Since 4 volts is a large energy to attribute to kinetic energy, the possibility that the ion is

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* The narrow peak observed for $\mathrm{SiCl_2^-}$ ions shows that this spread is about 1.5 volts.

* The attempt to explain the 11.8-volt value, as caused by the process $\mathrm{SiCl_4 \rightarrow SiCl_2^+ + Cl + Cl^-}$, requires that $I(\mathrm{SiCl_2}) \leq 9.7$ volts. It is then impossible to explain the 18.4-volt value, since dissociation to $\mathrm{SiCl_2^+ + 2Cl}$ would leave about 3 volts excess energy but still not enough for the 3.5 volt excited state of $\mathrm{SiCl_2}$.

[14] R. Schwarz and U. Gregor, Zeits. f. anorg. allgem. Chemie **241**, 395 (1939).

TABLE II. Comparison of $SiCl_4$ with CCl_4.

Dissociation products	Appearance potential (volts)	Relative intensity at 75 v
CCl_4^+	11 ±1.0	0.02
$CCl_3^+ + Cl^-$	12.2±0.2	100
$SiCl_4^+$	11.6±0.2	56
$SiCl_3^+ + Cl^-$	12.9±0.2	4–100

produced by transitions to levels *h* or *g*, which would result in 2.5 or 5 volts more kinetic energy, is ruled out. Furthermore it indicates that $D(SiCl_4)$ is at least 14.8 volts, rather than the lower value obtained by Asundi, Karim, and Samuel,[12] using the lower value of the heat of sublimation of silicon.[15]

It is noticed that all processes except that producing $SiCl^+$ are identified with reasonable certainty as caused by dissociation into the greatest number of products. Thus the third Cl^- peak was explained as due to production of $SiCl+2Cl+Cl^-$, rather than $SiCl+Cl_2+Cl^-$. Similarly the second appearance potential for $SiCl_2^+$ involves the extra chlorine atoms in the free state rather than as a molecule, and the Si^+ ions are accompanied by four free chlorines rather than chlorine molecules. Even in the doubtful case of $SiCl^+$ the evidence favors the process resulting in $SiCl^+ + 3Cl$ rather than $SiCl^+ + Cl_2 + Cl$. This effect was noticed by Smith[16] working with methane, although with silicon tetrachloride it is rather to be expected, since the $Cl-Cl$ distance in silicon tetrachloride is so great (3.27A) that the attractive force between the two atoms is very small. (The $Cl-Cl$ distance in Cl_2 is only 2A.)

A striking contrast between the dissociation processes in carbon tetrachloride and silicon tetrachloride is the relative probability of processes of the type $MCl_4 \rightarrow MCl_4^+$ and $MCl_4 \rightarrow MCl_3^+ + Cl^-$. The appearance potentials and relative probabilities at 75 v electron energy are shown in Table II.* Presumably the large error in $A(CCl_4^+)$ is caused by the small ion current. The range in intensities for $SiCl_3^+ + Cl^-$ is because of the uncertainty in ion collecting efficiency of the mass spectrometer used for $SiCl_4$. It is seen that ion pair production is relatively much more probable in carbon tetrachloride. This is not unexpected from the fact that carbon tetrachloride has simple valence binding, while the binding in silicon tetrachloride is partially double-bond and partially ionic in character[17] and hence should be stronger. A further consequence of the double bond character of silicon tetrachloride binding is that some of the relatively unstable *d* orbitals of silicon must be used to accommodate the extra electron pair in the double bond, whereas only the *s* and *p* orbitals are used in carbon. This should make removal of an electron from silicon tetrachloride easier than from carbon tetrachloride. Although these qualitative arguments agree with the observed ion intensities at 75 volts, the energies at which each process is observed do not. Using the probable values from Table II, the energy difference for the two processes in carbon tetrachloride is 1.2 volts while in silicon tetrachloride it is 1.3 volts. Hence the probability that a process occur must depend more strongly on factors other than the minimum energy required.

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[15] *International Critical Tables.*

[16] L. G. Smith, Phys. Rev. **51**, 263 (1937).

* Data for CCl_4 are from reference 7.

[17] L. C. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).