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Electronegativity

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The energies of positive and negative ions relative to the neutral atoms are conveniently and accurately expressed for a given atom by a power series in $N = n - Z$, where n = the number of electrons around the nucleus in a given ionization state and Z = the atomic number of the nucleus. For a neutral atom the electronegativity is defined as $\chi = (-dE/dN)_{N=0}$ where dE is the energy change which accompanies the change in charge dN and should be expressed in the units energy per electron. Similarly the value of $(-dE/dN)_{N=-1}$ represents the electronegativity of the singly charged positive ion. The $E(N)$ curve exhibits a discontinuity in slope at N values where there is a transition from one type of atomic orbital to another. If only the first ionization potential and the first electron affinity are known for a given species, $\chi = (-dE/dN)_{N=0}$ is equivalent to the well-known Mulliken relationship that electronegativity is equal to the average of the ionization potential and the electron affinity.

Introduction

The qualitative aspects of electronegativity are readily comprehensible. In a diatomic molecule, the atom which has a net negative charge compared to the other atom is said to be more electronegative. The specification of the electronegativity of an atom (in a given valence state) on this qualitative basis would amount to a specification of its position in an ordinal listing of the elements, such that it would be negative in a diatomic molecule formed with any element listed below it. Similarly the criterion for setting up such a list of the atoms in the order of their electronegativity would be the polarity, but not the amount of the partial ionic character of diatomic molecules, of which the nuclear quadrupole coupling constant is an imperfect measure.

The quantitative aspects of electronegativity are less clear. Quantitatively, electronegativity is defined as the tendency of an atom in a molecule to attract electrons.¹ Gordy^{2,3} found a correlation of electronegativity with Z^*/r_{cov} , where Z^* is the effective nuclear charge acting on the outermost electrons, and r_{cov} is the covalent radius of the atom. Gordy took this correlation as a demonstration that the physical quantity corresponding to the term electronegativity was the potential

due to the partially screened nuclear charge at the covalent radius. Allred and Rochow⁴ found a good correlation of electronegativity with Z^*/r_{cov}^2 and indicated that electronegativity represented a force on the atomic electrons at the covalent radius. Other correlations⁵ have been made with still other powers of r . Mulliken's⁶ values represent an average of the binding energy of the outer electrons in an atom and its corresponding negative ion. Mulliken's view introduces the idea that electronegativity represents an average of a property over a range of ionization instead of being solely a property of the neutral atom. Other approaches relate electronegativity to a variety of other properties.⁶⁻⁸

After so many approaches, there is some confusion as to what physical picture corresponds to the term electronegativity. This confusion is also manifest in the question of what should be the units of electronegativity. It is difficult to understand the meaning of a quantity if one does not know in what units it is to be expressed. As shown in Table I, the electronegativities obtained by different investigators have different units. Clearly, the absolute numerical values of quantities having different units are not comparable, because they

(1) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1960, p. 88.
(2) W. Gordy, *Phys. Rev.*, **69**, 604 (1946).
(3) Cf. H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

(4) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).
(5) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).
(6) A. D. Walsh, *Proc. Roy. Soc. (London)*, **A207**, 13 (1951).
(7) W. J. Gordy, *J. Chem. Phys.*, **19**, 792 (1951).
(8) R. T. Sanderson, *ibid.*, **23**, 2467 (1955).

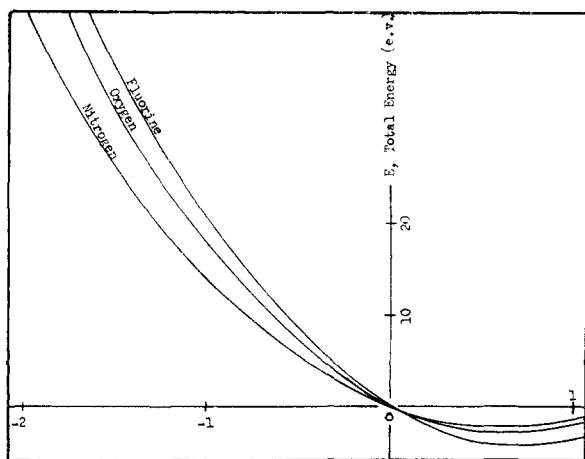


Fig. 1.—Atomic energy change with degree of ionization.

represent conceptually different entities. It would thus be desirable to have a defining equation based clearly on a physical concept which is in harmony with the definition of electronegativity and to clarify the question of units.

TABLE I
UNITS OF ELECTRONEGATIVITY

Pauling ¹	$(\chi_A - \chi_B) = 0.208 \{D(AB) - (1/2) [D(A_2) + D(B_2)]\}^{1/2}$	(Energy) ^{1/2}
Mulliken ⁵	$\chi_A = (I_A + I_{A-})/2$	Energy
Allred and Rochow ⁴	$\chi_A = e^2 Z_{\text{eff}} / r_{\text{cov}}^2$	Force
Gordy ²	$\chi_A = e Z_{\text{eff}} / r_{\text{cov}}$	Energy/electron
Walsh ⁶	$\chi_A = \text{force constant of AH molecule}$	Force/distance
Gordy ⁷	$\chi_A - \chi_B = 2$ (fraction ionic character)	Dimensionless
Sanderson ⁸	Ratio of av. electron density to that of corresponding rare gas atom	Dimensionless

Relation of Extrapolation of Ionization Potentials to Electronegativity.—Recent attempts to obtain electron affinities from the extrapolation of ionization potentials have been reasonably successful. In particular, the form

$$E(N) = aN + bN^2 + cN^3 + dN^4 \quad (1)$$

has been shown to be a good approximation to the true equation for representing the energy of atoms in various states of ionization. When this form is used in an extrapolation procedure to determine the electron affinities of fluorine, chlorine and oxygen, from their successive ionization potentials, very nearly the correct values are obtained. Typical plots are like those shown in Fig. 1, except that (1) the values shown in Fig. 1 represent the energy of the valence state for each atom or ion, while the others⁹ represent the average energy of all the states of the ground state configuration, and (2) in setting up Fig 1, the curve fitting was done using the electron affinity as an experimental point.

The ordinate, E , represents the total energy of all the electrons around a nucleus of atomic number

(9) H. Hellman and M. Mamotenko, *Acta Physicochim. URSS*, **7**, 127 (1937); J. L. Margrave, *J. Chem. Phys.*, **22**, 636, 1937 (1954); H. O. Pritchard and H. A. Skinner, *ibid.*, **22**, 1936 (1954).

Z , taking the energy of the neutral atom to be zero. The abscissa, N , represents the number of electrons present around the nucleus minus the atomic number, i.e., $N = n - Z$, where n is the number of electrons around the nucleus at any particular state of ionization. Thus, zero corresponds to the neutral atom, F ; one corresponds to the negative ion, F^- ; minus one corresponds to the singly ionized atom, F^+ ; etc. For $N = 1$, E is minus the valence state electron affinity; for $N = 0$, E is zero; for $N = -1$, E is the first valence state ionization potential; for $N = -2$, E is the sum of the first and second valence state ionization potentials; etc. Mulliken⁵ has pointed out the importance of using the ionization potentials corresponding to the appropriate valence state of the atom in a molecule.

In a molecule, the charge on an atom is increased or decreased due to the net increase or decrease in the time that electrons (some of which are originally from the other atom) spend on it. Thus for an atom in a molecule the quantity $(-N)$ represents the net charge on the atom, expressed in terms of fractions of an electronic charge. If a curve in Figure 1 is interpolated for fractional as well as integral values of N , then it may be taken to represent how the energy of an atom in a molecule would change as it gains or loses fractional electronic charge to the other atom, assuming that, except for the change in valence state, the atoms retain the same properties that they possess in their isolated state.

An atom, for which the E vs. N plot has a given slope at the origin $(-dE/dN)_{N=0}$, will take electrons away from any atom which has a smaller slope, because in the process of doing so, the energy of the system as a whole will be lowered. Since this is the behavior of a more electronegative atom toward a less electronegative atom, one may identify the term electronegativity with this slope: $\chi = (-dE/dN)_{N=0}$. Similarly, the electronegativity of an ion would be given by the slope of the curve corresponding to that ion; e.g., $\chi_{Cl^+} = (-dE/dN)_{N=-1}$.

Electronegativities of C, N, O, F, Si, P, S and Cl.—The coefficients in equation 1 were determined from the successive ionization potentials and the electron affinity. For fluorine, chlorine, oxygen and sulfur, the coefficients were determined by the method of averages,¹⁰ but the curve was caused to go precisely through the origin and the experimental points at $n = 1$ and $n = -1$. For fluorine and chlorine, there are enough data to define the curve through $N = -5$, and for oxygen and sulfur, through $N = -4$. For nitrogen and phosphorus, there are only enough data to determine one set of coefficients, and for carbon and silicon, there are still fewer items of data so that only terms up through the third power in equation 1 were used. The values of the coefficients are presented in Table II. It can be seen that virtually the entire contribution to E comes from the first and second powers of N and that higher terms contribute only a minor amount.

(10) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co. New York, N. Y., 1956, p. 516.

TABLE II

Element	COEFFICIENTS FOR EQUATION 1			
	a	b	c	d
F	-12.66	8.70	0.40	-0.083
O	-9.26	7.63	-.32	.002
N	-7.16	6.21	-.46	-.01
C	-5.00	5.59	.37
Cl	-9.83	5.65	.36	-.0433
S	-7.40	5.08	-.035	-.022
P	-6.37	4.47	.16	-.082
Si	-4.28	3.38	-.28

In Table III, the electronegativities determined from $(-dE/dN)_{N=0}$ are compared with electronegativities for the same valence state as given by Mulliken's method. For C, N, O, F and the corresponding elements of higher rows, the E vs. N curve can be defined for an appreciable range of N , because it represents a region corresponding to the successive ionization of several electrons, all of which are of the same type, viz., the p electrons. The E vs. N curve has a discontinuity in slope at a point which represents a transition from the ionization of p electrons to the ionization of s electrons, viz., the point $N = -1$, for the alkali metal atoms. As a result, for the alkali metal atoms, there are only three points on the E vs. N curve for the outermost s-orbital, $E(1)$, $E(0)$ and $E(-1)$ which are obtainable from the first ionization potential and the electron affinity. With only these three points, the determination of the constants in the equation $E(N) = aN + bN^2$ shows that the value of $(-dE/dN)_{N=0}$ reduces to exactly $(1/2)(I_A + I_{A-})$ which is Mulliken's formula and emphasizes the close relationship of the present method to that of Mulliken.

TABLE III
PURE p-ORBITAL ELECTRONEGATIVITIES

Element	Valence state	This work	Mulliken
		$(dE/dN)_{N=0}$, e.v./electron	$(1/2)(I_A + I_{A-})$,
F	s^2x^2yz, V_1	12.66	12.26
O	s^2x^2yz, V_2	9.26	9.58
N	s^2xyz, V_3	7.16	7.62
C	s^2xy, V_2	5.00	5.58
Cl	s^2x^2yz, V_1	9.83	9.47
S	s^2x^2yz, V_2	7.40	7.43
P	s^2xyz, V_3	6.37	6.2
Si	s^2xy, V_2	4.28	4.56

The values of electronegativity presented here are also like those of Mulliken in that they refer only to the lowest valence state of the atom. The same procedure could be applied to higher valence states if more data on higher ionization potentials were available. In order to obtain values for electronegativity of use in practical chemistry, it is necessary to add together contributions from all the valence states, each weighted according to its per cent. of participation in the actual hybridized bonds.⁵

For the rare gases, the point $N = 0$ corresponds to a transition from the ionization of p-electrons to the ionization of s-electrons, and therefore the curve has a discontinuity in slope at $N = 0$, having a very steep slope for negative N and (assuming the electron affinity to be zero) a zero slope

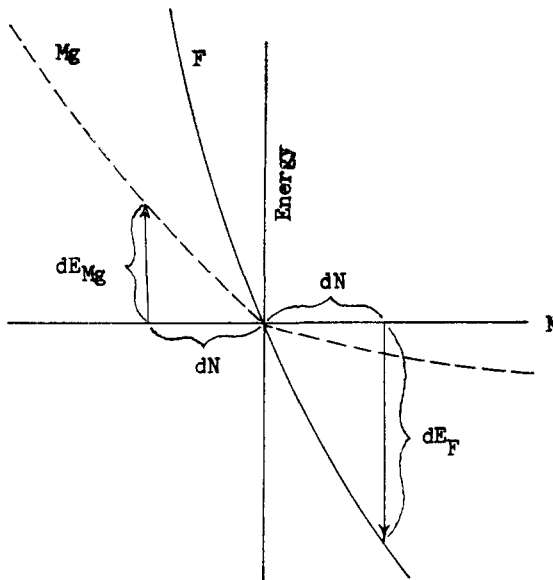


Fig. 2a.—Behavior of Mg toward F in the molecule MgF.

for all positive N . Thus, $(-dE/dN)$ is not well-defined at $N = 0$, and the rare gases show a peculiar dual behavior toward electron exchange, having little tendency to give away electronic charge (which may be correlated with the steep slope at negative N) and little tendency to take it up (indicated by the essentially zero slope at positive N).

In contrast, the E vs. N curve for Mg should show qualitatively three distinct regions of decreasing slope depending on whether a p-electron is being added to make $Mg^-(N > 0)$, least slope); s-electrons are being removed to make Mg^+ or Mg^{++} ($-2 < N < 0$, intermediate slope); or p-electrons are being removed to make Mg^{+++} and higher ions ($N < -2$, largest slope).

Figure 2a shows qualitatively the behavior of Mg with a highly electronegative atom, F. One can see that for a small displacement of electronic charge, dN , from Mg to F, the decrease in energy of the fluorine atom, dE_F is greater than the energy increase for the Mg atom, dE_{Mg} . Therefore, such a transfer will make the molecule MgF more stable. This represents the behavior of Mg toward an atom having $(-dE/dN)_{N=0}$ greater than the larger of the two limiting slopes of Mg at $N = 0$.

Figures 2b and 2c show qualitatively the behavior of Mg toward an atom, Cs, having a value of $(-dE/dN)$ less than the larger limiting slope for Mg at $N = 0$. The curves for Mg are drawn on the assumption that the electron affinity of Mg is much less than the electron affinity of Cs. This is reasonable because the extra electron would be strongly shielded by two outer s-electrons in Mg. In this case the two curves do not cross, and therefore in MgCs, Mg would exhibit behavior like that of the rare gases toward exchange of electronic charge. Figure 2b shows that electronic charge cannot be shifted from Cs to Mg, because the energy decrease produced by the charge residing on Mg does not offset the energy increase incurred by taking the charge away from Cs. Figure 2c shows by the same reasoning that electronic charge cannot be shifted from Mg to Cs. The

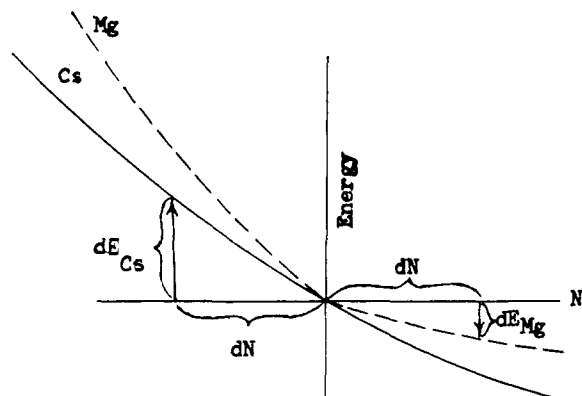


Fig. 2b.—Behavior of Mg toward Cs in the molecule MgCs.

electronegativity of Mg may be taken as the larger of the two limiting slopes at $N = 0$. Mg will be positive when combined with elements having a greater electronegativity. However, in contrast to most atoms which are negative, when combined with elements having a lower electronegativity, one expects Mg in molecules like MgCs to show no appreciable tendency to form a negative ion. Thus, such molecules should show a very small ionic component in their binding and behave much like homonuclear diatomic molecules.

Discussion

According to the previous analysis, the units of electronegativity should be energy per electron. The quantity $(-dE/dN)_{N=0}$ fulfills the desiderata for an adequate interpretation of the definition, "tendency of an atom in a molecule to attract electrons." The result of a small charge dislocation on interaction of two atoms is that the energy of the more electronegative atom is decreased by a larger amount than the energy is increased for the other atom, and therefore the molecule can lower its energy very simply by transferring charge from one atom to the other. It should be noted that the energy change under discussion is not that which accrues from the electrostatic attraction between the newly formed ions. The electronegativity is a property which is characteristic of the internal constitution of an atom and the ions which can be formed from it. For example, the outer s-electron of an alkali metal atom is less tightly bound than the p-electron in a halogen atom. This results from the fact that the s-electron of the alkali metal atom is forced by the Pauli principle into an orbital where it is strongly shielded by all of the inner electrons, while the p-electrons in a halogen atom are only weakly shielded by each other. The energy change under discussion results from the fact that the s-electron can spend part of its time in the lower energy region around the halogen atom.

In a screening constant theory of atoms, the binding energy of electrons tends to behave approximately like $E \approx -R(Z^*)^2/n^2$, where R is the Rydberg constant, while the atomic radius, which corresponds to the outermost maximum in the wave function behaves approximately like $r \approx a_0(n^2/Z^*)$, where a_0 is the Bohr radius.¹¹ This

(11) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York, N. Y., 1953, p. 81.

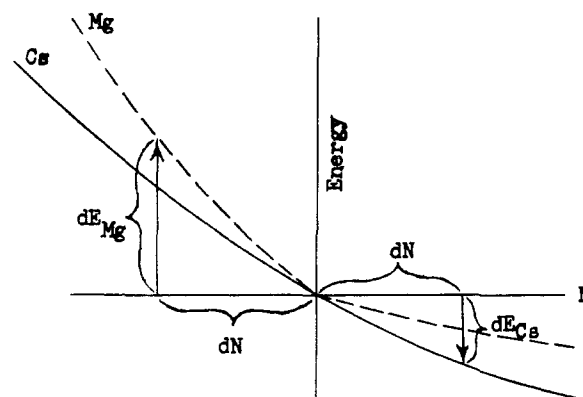


Fig. 2c.—Behavior of Mg toward Cs in the molecule MgCs.

implies that the binding energy of an electron and the atomic radius tend to change in a regular and related manner in going from one atom to another. The periodic table shows many regularities, and it is not surprising that many correlations can be found between seemingly unrelated quantities. This is probably the basis for the correlations between electronegativity and atomic radius. Though these correlations may be extremely useful, it is hard to find one among them which would qualify as the fundamental measure of electronegativity. This may also be the basis of Pauling's scale, as it is difficult enough to imagine a physical quantity corresponding to the unit, square root of energy, much less to see that it truly reflects a tendency to attract electrons.

The methods based on partial ionic character must also be considered to be secondary measures of electronegativity. Although the amount of partial ionic character of a bond may be expected to parallel closely the difference in electronegativity of the two atoms, the relation between these quantities is not exact. The electronegativity represents an intensity factor in taking away the first small amount of charge from the other atom, while partial ionic character represents both the intensity and capacity factors for the atoms to give away or absorb appreciable amounts of charge.

When one says the Li is more electronegative than Na, he implies that Li will take electronic charge away from Na in the molecule LiNa; however, we have no assurance that the molecule NaI will have a higher ionic character than the molecule LiI. Evidence points to the fact that LiI is more ionic than NaI.¹² Although Na may have a lower intensity for attracting electrons than Li, it does not necessarily have a greater capacity to give away a large quantity of charge. This lack of correlation between difference in electronegativity and partial ionic character may be even more exaggerated in comparing atoms of different columns of the periodic table, e.g., oxygen and bromine.

The present approach and that of Mulliken are similar in that the present method reduces to that of Mulliken when only the electron affinity and the first ionization potential are considered. The difference in units between those given by the

(12) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

present method and those given by Mulliken is illusory, since ionization potential and electron affinity, though usually expressed in units of energy,

have an implied unit: per electron, because they represent the energy change which accompanies the removal or addition of one electron.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

The Influence of Phase, Temperature and Bromine Concentration on Bromine Production in the Decomposition of CCl_3Br by γ -Rays^{1a,b}

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The production of Br_2 by the radiolysis of CCl_3Br with Co^{60} γ -rays has been studied in the solid, liquid and gas phases and as a function of temperature and bromine concentration. In the solid state at -121° and below, the value of $G(\text{Br}_2)$ is 0.12 molecule produced/100 e.v., independent of temperature. From -78 to 98° $G(\text{Br}_2)$ increases with temperature to about 3.5 with an apparent activation energy of about 2 kcal./mole. Although this activation energy suggests a diffusion controlled process, there is no change in $G(\text{Br}_2)$ or its temperature dependence on crossing solid phase transitions at -35.5 and -13.5° or in going from the solid to the liquid state at the melting point -5.6° . Preliminary experiments indicate that there is no marked difference in yield in the gas phase as compared to the liquid phase at the boiling point. At bromine concentrations above about 0.01 M , $G(\text{Br}_2)$ is independent of bromine concentration at all temperatures in both the solid and the liquid. Below 0.01 M and at temperatures of 20° and above, however, $G(\text{Br}_2)$ decreases with increasing concentration. The bromine-sensitive reaction appears to have an activation energy of about 3 kcal./mole, slightly higher than the bromine insensitive reaction. The presence of oxygen raises $G(-\text{CCl}_3\text{Br})$ several-fold, the production of Cl_2 (a minor radiolysis product) being increased by a larger factor than Br_2 production.

Introduction

This paper reports investigations of the effects of phase, temperature and radical scavengers on the radiolysis of CCl_3Br , with particular reference to the yield of bromine in the liquid and solid phases. It is part of a more extensive investigation which has included² a comparison of the photochemical and radiation induced decomposition of CCl_3Br and the exchange of CCl_3Br with Br_2 in the gas and liquid phases. In the latter work² five organic products, CCl_4 , CCl_2Br_2 , CClBr_3 , C_2Cl_6 and $\text{C}_2\text{Cl}_5\text{Br}$, have been observed and their yields have been followed with the aid of gas chromatography.

These studies were designed to obtain information which would contribute to an understanding of the mechanisms of radiolysis of organic compounds. CCl_3Br was chosen because of its simplicity, because of the ease of following its decomposition by measurement of the bromine produced and because information was already available on its thermal³ and photochemical⁴ reactions and its reactions after activation by nuclear processes.⁵

Experimental

General Methods.—All irradiations of liquid and solid CCl_3Br were made on samples of about 5 ml. contained in

an annular vessel surrounding a 40 curie Co^{60} γ -ray source.⁶ Attached to the annular vessel at a distance sufficient to prevent troublesome darkening by irradiation was a cell made of square Pyrex tubing of 1 cm.² cross section. By pouring the liquid into this cell the optical absorbance of the liquid could be measured periodically with a spectrophotometer without opening the purified, air-free sample to the air.⁶ Thermostating media used in maintaining desired temperatures during irradiations included: liquid air, -190° ; liquid-solid butyl chloride, -121° ; Dry Ice-acetone, -78° ; liquid-solid anisole, -37° ; Dry Ice-acetone-aniline, -12° ; ice-water, 0° ; thermostated mineral oil-bath, temperatures above 20° .

Dosimetry.—Dosage rates were determined by measurement of the Fe^{+++} yield in air-saturated water solutions of ferrous ammonium sulfate, 0.8 N in H_2SO_4 , under irradiation conditions identical with those used for irradiation of CCl_3Br . It was assumed that the molar absorptivity index of Fe^{+++} is 2130 at 305 $m\mu$ and 25° and that 15.6 Fe^{+++} ions are formed per 100 e.v. absorbed.⁷ Energy absorption in CCl_3Br was determined from that in the dosimeter solution by use of the calculated ratio of the mass absorption coefficients of CCl_3Br and water for Co^{60} γ -rays. The value of this ratio is 1.12.

Sample Preparation.— CCl_3Br from the Michigan Chemical Corporation, containing 0.1% glycidyl phenyl ether as a preservative, as well as other impurities, was purified by the following steps: vigorous mechanical stirring with successive portions of concentrated H_2SO_4 until no discoloration of the acid occurred on several hours of additional stirring; washing with Na_2CO_3 and water, drying with CaCl_2 and P_2O_5 ; illumination with a 1000 watt projection lamp at 6 inches for 10 hr. after making 0.01 M in Br_2 ; passage through a 30×1.5 cm. column of activated alumina; fractional distillation through a 12" Vigreux column; passage of the middle third of the distillate through a fresh activated alumina column. A similar procedure omitting the H_2SO_4 and alumina treatments gave a product which yielded radiolysis results indistinguishable from those on material prepared by the more extensive procedure. CCl_2Br_2 (Michigan Chemical Corp.), used as a carrier for small quantities of radioactive CCl_2Br_2 , was prepared for use by fractional distillation in a Vigreux column at 43° under 27 mm. pressure.

The irradiation vessels were prepared for filling by allowing them to stand filled with alcoholic KOH for an hour, following which they were rinsed, allowed to stand in boiling

(1) (a) Presented before the Division of Physical and Inorganic Chemistry at the April, 1955, meeting of the American Chemical Society in Cincinnati, Ohio. (b) This work is reported in greater detail in the Ph.D. thesis of Richard F. Firestone, University of Wisconsin, 1954.

(2) A. H. Young, Ph.D. thesis, University of Wisconsin (1958), available from University Microfilms, Ann Arbor, Michigan.

(3) (a) A. A. Miller and J. E. Willard, *J. Chem. Phys.*, **17**, 168 (1949); (b) N. Davidson and J. H. Sullivan, *ibid.*, **17**, 176 (1949); (c) E. Becker, Ph.D. thesis, University of Wisconsin, 1953.

(4) (a) E. Paterno, *Jahresb. Forts. Chem.*, **24**, 259 (1871); (b) W. Noddack, *Z. Elektrochem.*, **27**, 359 (1921); (c) H. Grusse, *ibid.*, **29**, 144 (1923); (d) H. G. Vesper and G. K. Rollefson, *J. Am. Chem. Soc.*, **56**, 1455 (1934); (e) W. Franke and H. J. Schumacher, *Z. physik. Chem.*, **B42**, 324 (1939); (f) W. U. Day, Ph.D. Thesis, University of Wisconsin, 1942.

(5) (a) S. Goldhaber, R. S. H. Chiang and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 2271 (1951); (b) S. Goldhaber and J. E. Willard, *ibid.*, **74**, 318 (1952).

(6) R. F. Firestone and J. E. Willard, *Rev. Sci. Instr.*, **24**, 904 (1953).

(7) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).