mium iodide at which the transference number would be zero calculated in this way is 0.20 mole/l. A concentration of 0.21 mole/l. is obtained if the second set of constants is used. These values are in as satisfactory agreement with the results of Redlich and Longsworth as could be expected in view of the difference in ionic strength.

This work was supported by a grant from the Wisconsin Alumni Research Foundation.

MADISON, WIS. RECEIVED APRIL 8, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Elementary Processes in Radiation Chemistry. II. Negative Ion Formation by Electron Capture in Neutral Molecules[1,2,3]

BY JOHN L. MAGEE AND MILTON BURTON

Ionization processes characteristic of radiation chemistry yield energetic electrons which are ultimately degraded to thermal energies in ionization and collision processes. Although negative ions can be produced without positive-ion formation by impact of energetic electrons on molecules, the yield of such processes is so small that they make practically no contribution to the over-all picture. Thermal electrons can yield negative ions either in simple capture or in dissociative capture processes. When conditions for negative ion formation are satisfactory, low energy electrons ($< {}^1/_8$ ev. in gases, ${}^1/_4$ ev. in liquids) disappear almost exclusively in formation of negative ions rather than in neutralization of positive ions. At usual irradiation intensities, common substances which give negative ions by thermal electron capture include oxygen, liquid water, alcohols, alkyl halides and, in general, all compounds in states in which they have low-lying vacant orbitals. For capture of thermal electrons in a dissociative process, the electron affinity of the ion produced must exceed the strength of the bond ruptured. In general, such processes tend to increase ion-pair yield, but certain clearly described exceptions exist.

Radiation chemical syntheses of ozone and of hydrogen peroxide show behavior characteristic of reactions in which the principal neutralization process involves negative oxygen ions. When a negative-ion source (*e.g.*, oxygen or water) is present as impurity in a substance of low ionization potential (*e.g.*, benzene), the principal neutralization reaction in a radiation-chemical process involves interaction of the negative ion of the former and of the positive ion of the latter. Resultant characteristic reactions may mask the normal radiation-chemical reaction of the uncontaminated principal constituent.

Water vapor captures thermal electrons without dissociation but solvation of the negative ion in liquid water confers large electron affinity and produces a situation conducive to capture accompanied by dissociation. Resultant anisotropic distribution and high concentration of positive and negative ions may have special consequences, particularly in biological systems.

1. Introduction

Free electrons and positive ions are produced when high-energy charged particles pass through matter. The kinds of positive ions and the energy distribution of the free electrons depend primarily upon the nature of the substance and to a lesser extent on the incident particle (*i. e.*, its charge, mass and energy).[4] The complete radiation-chemical mechanism, which describes in detail all the chemical reactions resulting from the irradiation, depends upon all ions and radicals produced.[5] One small, but important, possible step in that mechanism is electron capture in the neutral molecule of the irradiated material. If capture is possible, large numbers of negative ions will form in the system, and neutralization will occur principally by positive–negative ion reaction. If capture is not possible in the neutral molecules, the free electrons will be thermalized and eventually recaptured in the positive ions which exist in the system.

In this paper we are considering in a general way negative ion formation by the electron capture mechanism only. We find it convenient to divide the discussion into four parts: (a) electronic states of negative ions; (b) cross section for electron capture as a function of electron energy; (c) energy distribution of free electrons in irradiated systems; (d) probability for capture of such free electrons. These topics are treated in the required detail. A discussion of capture possibilities in real systems with possible radiation chemical effects follows thereafter.

In this paper we are not concerned with formation of negative ions in the primary radiation chemical act, *e. g.*

$$RX \rightsquigarrow R^+ + X^-$$

either by the action of the primary charged particle or by action of fast secondary electrons. Our concern is exclusively with negative ion formation by electron capture and the consequences of such a possible process.

2. Electronic States of Molecular Negative Ions

2.1. Negative Ions of Singly Bonded Diatomic Molecules.—Most atoms are able to form negative ions because they have an electron affinity *i. e.*, the reaction

$$A + e \longrightarrow A^-$$

is exothermic. A few, of course, have zero or negligible affinity. Molecules are more complicated systems. Most of them have stable negative ion forms[6]; thus, dissociation from the lowest energy state of such ions is always endothermic. It is an important fact that the stable form is not necessarily attainable directly by electron capture (see the case of hydrogen[3]). Whether or not such attainment is possible depends upon the nature of the potential curves for the negative ion. The purpose of this section is the examination

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[1] Presented at the September 1949 meeting of the American Chemical Society, Atlantic City, N. J.

[2] A contribution from the Radiation Chemistry Project, operated by the University of Notre Dame under Atomic Energy Commission contract No. AT(11-1)-38.

[3] Paper I of this series: THIS JOURNAL, **72**, 1965 (1950).

[4] H. A. Bethe, "Handbuch der Physik," Vol. 24, pt. 1, Julius Springer, Berlin, 1933.

[5] M. Burton, *Ann. Rev. Phys. Chem.*, **1**, 113 (1950).

[6] H. S. W. Massey, "Negative Ions," Cambridge University Press, 1938.

of the more important features of these potential curves.

The simplest case is H_2^-. This system has been discussed by the authors[3] and a detailed calculation using the variational method has been made by Hirschfelder.[7] The two potential curves for H_2^-, both dissociating into H + H^-, are easily understood qualitatively in terms of molecular orbitals.[6] In its ground state the H_2 molecule has its two valence electrons in the lowest (bonding) molecular orbital. When the molecule adds an electron to form H_2^-, the added electron can go to the next higher (anti-bonding) orbital. A second electron arrangement, which involves only the same two molecular orbitals, places one electron in the bonding orbital and two electrons in the anti-bonding orbital. Clearly the energy for this state is higher than the first, and this is actually the lowest excited state of the ion. The higher potential energy curve in Fig. 1 represents a curve of this type. Electron capture into it requires the simultaneous excitation of one of the valence electrons of the molecule. This capture is an illustration of what is called a dielectronic process, because two electrons are involved.

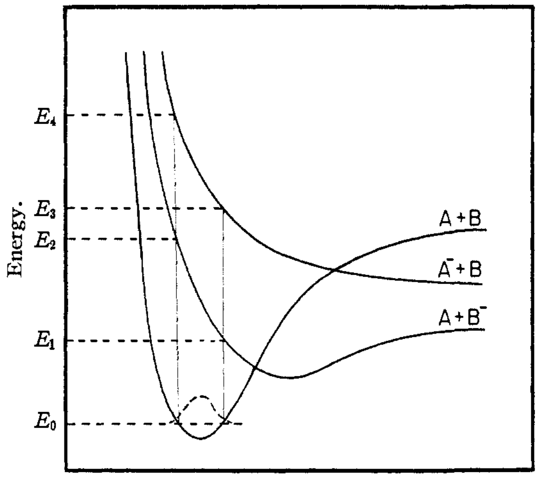

Fig. 1.—Negative ion potential curves for a molecule AB.

The potential energy curves of Fig. 1 demonstrate a case in which it is impossible to reach the negative ion of the molecule directly by electron capture. The Franck–Condon principle requires that the resulting state of that negative ion has energy E_1 to E_2, Fig. 1, above its dissociation limit. Thus, the newly formed ion dissociates immediately. The stable state of the negative ion of a molecule such as H_2^- can be formed by one of the reactions[8]

$$H_2' + e \longrightarrow H_2^- \qquad 2.1\ (1)$$

$$H^- + H_2 \longrightarrow H_2^- + H \qquad 2.1\ (2)$$

$$H + H^- + M \longrightarrow H_2^- + M \qquad 2.1\ (3)$$

Reaction (1) simply cannot occur at ordinary temperatures. The high activation energy of reaction (2) likewise eliminates it as a significant possibility. The three body reaction (3) is improbable. Therefore, the molecular ion would not be formed to any appreciable extent in an irradiated system. We shall see later that the number of H^- ions formed in irradiated hydrogen gas is negligible, so that there is a second reason for the unimportance of H_2^- in the radiation chemistry of hydrogen.

In general, the potential curves of all other negative ions, including diatomic, will be more complicated than those of H_2^-. The number of electronic states and their types will depend upon the molecular orbital structure of the system. The positions of each of the dissociation limits depends upon the electron affinity of the fragment concerned. The calculation of a complete potential curve is a complicated matter. No reported attempt has been made for a system other than H_2^-.

Probably, most electron capture phenomena involving single bonds can be understood on the basis of sets of potential curves of the type shown in Fig. 1. From data of the types indicated above one can draw approximate curves for a given bond. Table I lists some electron affinities, I_-, and Table II gives some energy data for single bonds. From them, approximate dissociation limits for the ions can be calculated. Some of the few available threshold values for electron capture appear in Table III. It is probable that deep minima in the potential curves go with high electron affinity for the two atoms, but quantitative relations are not known. In principle, the electron capture cross-section as a function of energy directly gives the potential energy of the ion for a configuration very nearly like the equilibrium configuration of the molecule (*cf.* the Frank–Condon principle).

TABLE I

SOME ELECTRON AFFINITIES[a]

Atom	I_-, e.v.	I_-, kcal. mole^{-1}
H	0.715	16.5
C	0.69	15.9
N	2.36	54.4
O	2.87	66.2
F	4.15	95.7
Cl	3.79	87.4
Br	3.68	84.9
I	3.53	81.4

[a] None of these affinities are experimental measurements. The value for hydrogen is from E. A. Hylleraas, *Physik*, **65** 209 (1930). It was calculated by the variational method. All others are given by R. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934). They are estimated for the appropriate valence states of the elements for single bonds.

If the bond under consideration is in a molecule more complicated than diatomic, the above remarks are only approximately valid (see section 2.4).

2.2. Negative Ions of Doubly Bonded Diatomic Molecules.—A double bond of great interest in radiation chemistry is that of the oxygen molecule. Bates and Massey[9] have examined the available data and have proposed two sets of potential energy curves for the ion each of which may be in agreement with the data. The fact that it

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[7] H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

[8] The symbol H_2' refers to a hydrogen molecule in a highly excited vibrational state.

[9] D. R. Bates and H. S. W. Massey, *Phil. Trans. Roy. Soc.*, **239**, 269 (1943).

TABLE II

SINGLE BOND DISSOCIATION ENERGIES IN KCAL. MOLE^{-1}

The quantities listed in the sections are successively: 1. Dissociation energy of bond X − Y.[a] 2. Heat of reaction $XY + e \rightarrow X + Y^-$. 3. Heat of reaction $XY + e \rightarrow X^- + Y$.[b]

X \ Y	H	C	N	O	Cl	Br	I
H	103.2 86.7			OH 103 36.8 86.5	102.1 14.7 85.6	83.0 −1.9 66.5	
C	CH_4 102[c] 85.5 86.1	C_2H_6 84.3[c] 68.4		CH_3OH 90.2[c] 24.0 74.3	CH_3Cl 73[f] −14 57	CH_3Br 68.5[d] −16.4 52.6	CH_3I 54.0[d] −27.4 38.1
N	NH_3 104[c] 87.5 49.6	CH_3NH_2 79[c] 63.1 24.6	N_2H_4 60[e] 6				
O	H_2O 114 97.5 47.8		150 95.6 83.8	117.2 51.0	44 −43 −22		
Cl					57.08 −30.3		
Br		C_2H_5Br 67[d] 51 −18			52.1 −35.3 −32.8	45.44 −39.5	
I	63.4 46.9 −18.0	C_2H_5I 54[c] 38 −27			49.63 −37.8 −31.8	41.89 −43.0 −39.5	35.55 −45.8

[a] Values for diatomic molecules were obtained from Gaydon, ref. 19; sources for bonds in polyatomic molecules are indicated. [b] Calculated with electron affinities of Table I. [c] H. A. Skinner, *Nature*, **158**, 592 (1946). [d] E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943). [e] M. Szwarc, *J. Chem. Phys.*, **17**, 505 (1949). [f] Adjusted to agree with CH_3–H.

TABLE III

APPROXIMATE THRESHOLD ENERGIES FOR ELECTRON CAPTURE BY GASEOUS MOLECULES[a]

Molecule	E_0(e.v.)	Molecule	E_0(e.v.)
H_2[b]	5	NO[c]	0
H_2O[c]	0	HCl[c]	0
O_2[c]	0	Cl_2[d]	0.25
SO_2[c]	0	Br_2[e]	.2
CO[c]	2	I_2[f]	.2
NH_3[c]	0.25		

[a] A discussion of the experimental methods and some of the results are found in H. S. W. Massey, "Negative Ions," Cambridge University Press, 1938. [b] Calculation by Hirschfelder. [c] N. E. Bradbury, *J. Chem. Phys.*, **2**, 827 (1934). [d] V. A. Bailey and R. H. Healey, *Phil. Mag.*, **19**, 725 (1935). [e] V. A. Bailey, R. E. B. Makinson and J. M. Somerville, *ibid.*, **24**, 177 (1937). [f] R. H. Healey, *ibid.*, **26**, 940 (1938).

was impossible for them to obtain a unique set of curves emphasizes the dearth of information regarding ions.

The feature of interest of O_2^- for radiation chemistry is that O_2 (as one may see from the curves of Bates and Massey) captures electrons without threshold energy. More mention of this will be made later. Also the reaction

$$O_2 + e \longrightarrow O + O^-$$

occurs for certain electron energies.

Another example of a double bond of interest in radiation chemistry is the ethylenic bond. Multiple bonds, because of their greater strength, tend to be more difficult to dissociate than single bonds. This factor may be important in the insensitivity to ionizing radiation of aromatic compounds and compounds containing "resonance" energy. The potential energy curve for the typical C–C single bond of ethane is not quite so deep. The threshold energy for electron capture (*i.e.*, $E_1 - E_0$ of Fig. 1) is expected to be approximately the same for the two cases. Although such threshold energy is generally sufficient for rupture of a single bond, it usually does not suffice for a double bond.

2.3. Negative Ions of Other Multiply Bonded Molecules.—There are no reported studies of other multiple bonds. In general, the values of neither $E_1 - E_0$ nor I_- (the electron affinity) are greatly different for different carbon compounds, or for the different radicals. The increase in the C≡C bond strength as compared with the C–C bond strength consequently makes even less likely the probability for electron capture in a dissociative process in such compounds.

2.4. Negative Ions of Polyatomic Molecules.—Very few general statements can be made about electron capture in complex molecules and so we shall consider the topic only briefly at this point. Almost any motion of the molecule involves the changing of many interatomic separations. Consequently, relatively simple potential curves cannot be drawn. However, in case one atom has considerably larger electron affinity than any other, it would seem that capture resulting in formation of its negative ion and dissociation of one of its bonds could be approximately represented by a transition to a curve such as the lowest one in Fig. 1. An example of this is an alkyl halide RX, which should capture electrons to form X^-. Other examples are

$$ROH + e \longrightarrow R + OH^-$$

$$R_1OR_2 + e \longrightarrow \begin{cases} R_1 + OR_2^- \text{ or} \\ R_2 + OR_1^- \end{cases}$$

In compounds containing many like atoms (*e.g.* hydrocarbons) and particularly those having resonance (aromatics), electron capture is not expected to result in the breaking of chemical bonds. One can see this qualitatively by noting that the electron tends to be shared by a number of different atoms and thus the forces tending to change the interatomic distances must act on many bonds. Since there is usually energy enough to break at most *one* bond and several bonds are involved, no dissociation is expected.

3. Capture Cross Section

Because of the Franck–Condon principle, in order for capture to occur the energy of the electron is restricted within certain limits. In Fig. 1, a schematic set of potential curves for the negative ion states of a single bond is given. The value of ψ^2 for the lowest state of the normal molecule AB is shown with the dotted curve; this gives, of course, the relative probability that the normal molecule will be found with a certain internuclear separation. Thus, it is clear that, if an electron is to be captured into the lowest ion state, its energy must be, for all practical purposes, within the limits E_1 and E_2. For capture into the higher state, the electron energy must be approximately between E_3 and E_4. It is clear, therefore, that the capture cross section must look qualitatively as indicated in Fig. 2.

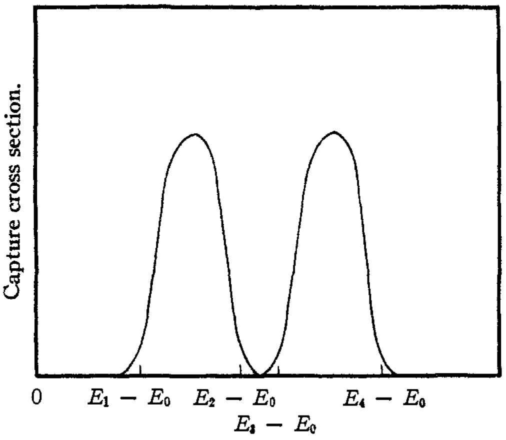

Fig. 2.—Electron capture cross section for the molecule AB as a function of energy.

Various experimental studies on electron capture have been made.[10-14] The numerical value of the cross section tends to be low. For most cases, at the maximum, the probability that the electron is captured in a collision is only about one part in 10^3 or 10^4.

4. Free Electrons

4.1. The Secondary Electrons Formed Directly by the Incident Particle.—Very few satisfactory measurements have been made on the spectrum of energies of electrons ejected by high velocity charged particles. The theory of the process is rather rough but it is usually considered more satisfactory than the limited measurements for obtainment of the energy spectrum. It cannot be said that theory and experiment agree; it is better to say that they do not disagree. Table IV gives the secondary electron spectra for incident electrons of several energies. These spectra do not differ greatly. They have approximately the same form for all high energy particles. A typical spectrum has the following characteristics: (a) *Half* the electrons ejected have energies less than about 5 ev. (b) The *average* energy given to an electron is about 70 ev. These two facts indicate that the distribution has a long high-energy "tail."

TABLE IV

CALCULATED SPECTRUM OF SECONDARY ELECTRONS FROM PRIMARY ELECTRONS OF VARIOUS ENERGIES (FROM REF. 4)

The figures in columns 2-5 give the percentages of secondary electrons having energies above the values indicated in column 1.

Energy of secondary electrons, ev.	Energy of primary electrons, ev. 10^3	10^4	10^5	10^6
0	100	100	100	100
3.39	66.9	64.6	62.9	61.1
6.77	49.0	45.1	43.9	41.6
13.54	31.1	27.4	26.2	23.9
27.1	17.4	14.7	14.0	12.2
40.6	12.1	10.0	9.7	8.2
67.7	6.6	5.4	5.7	4.7
135.4	2.5	3.1	2.6	2.2

4.2. Effect of Secondary Electrons.—In an energy region in which an ionization process is possible, its cross section is likely to be much higher than any other cross section. It is therefore rather certain that the most energetic electrons will produce much additional ionization. Those electrons having sufficiently high energy will produce several other electrons, the average spectrum of which in the low energy range (*i.e.*, below the cut-off set by the energy of the incident electron will be very similar to that of electrons produced by the original high energy particle.

4.3. The Low-energy Free Electron Spectrum.—Our previous considerations have made clear that only the relatively low-energy free electrons can be captured. For estimations of capture probability we need a spectrum of electron energies in the low-energy region (*i.e.*, below the ionization potential of the substance under study). By "spectrum" we now mean the distribution of energies which electrons have when they first appear in the low energy region (not necessarily the distribution of energies they have when they are first produced). Clearly a theoretical or experimental spectrum is extremely difficult to obtain. We make the assumption that this net spectrum is the same as the low-energy portion of that of the primary particle described in section 4.1. Although this is only an assumption, it can be supported by semi-quantitative appeals to theory, *cf.* arguments by Bethe.[15]

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(10) N. E. Bradbury, *J. Chem. Phys.*, **2**, 827 (1934); N. E. Bradbury and H. E. Tatel, *ibid.*, **2**, 835 (1934).

(11) V. A. Bailey and R. H. Healey, *Phil. Mag.*, **19**, 725 (1935).

(12) V. A. Bailey, R. E. B. Makinson and J. M. Somerville, *ibid.*, **24**, 177 (1937).

(13) R. H. Healey, *ibid.*, **26**, 940 (1938).

(14) H. D. Hagstrum and J. T. Tate, *Phys. Rev.*, **59**, 354 (1941).

(15) H. A. Bethe, *Ann. Physik*, **5**, 325 (1930).

We find that an analytical expression which reproduces the low energy spectrum satisfactorily is

$$f(\epsilon) = \frac{8}{3(1+\epsilon/I)^3}\cdot\frac{1}{I} \qquad (1)$$

where ϵ is the energy, $f(\epsilon)$ is the fraction of free electrons per unit energy interval, and I is the ionization potential of the molecule of the medium. From the definitions it is clear that the integral of $f(\epsilon)$ is unity, *i.e.*

$$\int_0^I f(\epsilon)\,\mathrm{d}\epsilon = 1 \qquad (2)$$

5. Capture Possibilities

5.1. Competition of Capture with Degradation.—We are interested in the probability for capture of free electrons of the spectral distribution described in the previous section. It is clear that an electron with a particular energy of formation ($0 \leq \epsilon \leq I$), has two possible fates: it is either thermalized or captured in a neutral molecule. We are considering cases in which the total ionization is sufficiently small that we can neglect capture by positive ions of electrons of greater than thermal energy. Also, we are considering only systems sufficiently large for complete thermalization of electrons before collision with walls. There may be important effects of geometry in small systems; consequently, our considerations apply only to essentially infinite media.

An electron having the energy ϵ has an average probability $h(\epsilon)$ for being captured on collision. Since it is being thermalized, it also loses a certain fraction of its energy $\lambda(\epsilon)$ per collision, on the average. For this consideration we assume that thermal energy, 1/40 ev., is essentially zero. If we take N electrons having a given energy, ϵ, the number captured in an average collision at that energy is $-\Delta N$, the average energy lost by those which are not captured is $-\Delta\epsilon$, and we have the relationship

$$\frac{-\Delta N}{-\Delta\epsilon} = \frac{h(\epsilon)N}{\lambda(\epsilon)\epsilon} \qquad (3)$$

which gives the number of the electrons which are lost by capture as the energy drops by the amount $-\Delta\epsilon$. Since these are small increments, we can conveniently treat (3) as a differential equation. If we have $h(\epsilon)$ and $\lambda(\epsilon)$ as a function of energy, then this equation can be solved numerically to find the fraction of electrons which survive as the energy is degraded to thermal (*ca.* zero). Explicitly, we have

$$\int\frac{\mathrm{d}N}{N} = \int_\epsilon^0 \frac{h(\epsilon)\mathrm{d}\epsilon}{\lambda(\epsilon)\epsilon} = \ln\frac{N(0)}{N(\epsilon)} \qquad (4)$$

Now let us make the definition

$$P(\epsilon) = 1 - \frac{N(0)}{N(\epsilon)} \qquad (5)$$

for the fraction of electrons starting at the energy ϵ which are captured during thermalization.

5.2. Probability for Capture During Thermalization.—Of the electrons formed by ionization processes during irradiation, the fraction captured P_c during thermalization is obtained by integrating $P(\epsilon)$ over the low energy electron spectrum where we continue our assumption that high velocity electrons are not captured in any significant number.

$$P_c = \int_0^I f(\epsilon)P(\epsilon)\mathrm{d}\epsilon \qquad (6)$$

Some experimental knowledge exists of the quantities $h(\epsilon)$ and $\lambda(\epsilon)$, which determine $P(\epsilon)$, in equation (3). For the purpose of orientation we consider a very simple case. *We shall find that in any case there is but little chance of electron capture in this process and that an elaborate calculation is unnecessary.*

Assume that $h(\epsilon)$ differs from zero in the low energy region only between E_1 and E_2 and is a constant in this region. That this situation is approximately true is shown by consideration of the cross sections shown in Fig. 2; each area there shown may be taken as rectangular in shape. We also assume for convenience that $\lambda(\epsilon)$ is a constant in this region. With these restrictions we can integrate (4) analytically. For electrons initially having the energy E_2 or greater

$$P(\epsilon) = 1 - \left[\frac{E_1}{E_2}\right]^{h/\lambda} \qquad E_2 \leq \epsilon \leq I$$

For electrons having initial energy, ϵ, between E_1 and E_2

$$P(\epsilon) = 1 - \left[\frac{E_1}{\epsilon}\right]^{h/\lambda} \qquad E_1 \leq \epsilon \leq E_2$$

Finally, for electrons having initial energies less than E_1

$$P(\epsilon) = 0 \qquad 0 \leq \epsilon \leq E_1$$

Thus, with the restrictions noted we have, from (1), (3) and the results just obtained

$$P_c = \frac{8}{3}\int_{E_1}^{E_2}\frac{1}{I}\left\{1 - \left(\frac{E_1}{\epsilon}\right)^{h/\lambda}\right\}\frac{\mathrm{d}\epsilon}{(1+\epsilon/I)^3} + \left\{1 - \left(\frac{E_1}{E_2}\right)^{h/\lambda}\right\}\int_{E_2}^{I}\frac{1}{I}\frac{\mathrm{d}\epsilon}{(1+\epsilon/I)^3} \qquad (7)$$

In Table V values of P_c are recorded for various values of the ratio h/λ and of the threshold energy E_1/I for the special case that $E_2 - E_1 = 0.2\ I$. This table makes clear that no capture mechanism with a very large threshold energy can capture an appreciable fraction of the free electrons regardless of the value of h/λ. A further conclusion is that the value of h/λ must be in the vicinity of unity or greater for capture to compete at all effectively with thermal degradation.

TABLE V

FRACTION OF ELECTRONS CAPTURED DURING THERMALIZATION AS A FUNCTION OF E_1/I.

E_1/I	h/λ				
	0.01	0.1	1.0	10.0	∞
0.01	0.025	0.225	0.878	0.971	0.98
.05	.012	.109	.619	.863	.88
.2	.003	.032	.244	.560	.59
.4	.001	.011	.091	.305	.35
.6	.0004	.004	.034	.147	.19
.8	.0001	.0008	.008	.046	.08

5.3. Rate of Thermal Electron Capture.—It follows from the previous considerations that the probability of capture processes with thresholds appreciably above thermal energy is effectively zero. Low-energy threshold processes involving neutral molecules may compete favorably with positive ions for capture of thermalized electrons under certain conditions. Here we investigate competition between electron capture by positive ions and a particular type of neutral molecule (*i*) present in a gas. The relative rates for the two captures y_i is given by

$$y_i = \frac{k_i N_i N_e}{k_+ N^+ N_e} = \frac{k_i N_i}{k_+ N^+} \tag{8}$$

where the *k*'s are the reaction rate constants and the *N*'s are the concentrations in numbers of molecules, ions or electrons per unit volume.

In order to carry the consideration further we must obtain N^+. An interesting (and convenient) case for gases is the steady state condition in which all concentrations are uniform in space. This case applies for low gas densities and small ionization densities along the particle tracks. (It is also applicable to consideration of high density tracks when attention is addressed to the microscopic features of the system.) Let us further assume that electron capture in the *i*th type neutral molecule is the principal way electrons are removed. Then we have

$$dN_e/dt \simeq R - k_i N_i N_e = 0 \tag{9}$$

$$dN_i^-/dt = k_i N_i N_e - k_i' N_i^- N^+ = 0 \tag{10}$$

as determining the steady state conditions, where R is the number of ionizations per unit time per unit volume, N_i^- is the number of negative ions of species *i*, and k_i' is the pertinent rate constant. Since, by assumption, the electrons are being removed at a much higher specific rate than the positive ions, we can say that

$$N_i^- \simeq N^+$$

thus

$$N^+ \simeq (R/k_i')^{1/2}$$

$$y_i \simeq \frac{k_i}{k_+} N_i \left(\frac{k_i'}{R}\right)^{1/2} \tag{11}$$

For the case we here consider this quantity must come out to be much greater than unity. When it is in the vicinity of unity, the assumptions have broken down and the positive ions can compete favorably with the neutral molecules for the free (thermal) electrons.

For k_i' we take 10^{-6} as order of magnitude.[16] The ratio k_i/k_+ is the ratio of cross sections for the two capture processes. It is well known[6] that if a threshold for capture exists, the cross section is usually $\backsimeq 10^{-20}$ near this threshold. On the other hand, the cross section for capture by the positive ion will be about 10^{-13} cm.^{2}. Thus we take

$$k_i/k_+ = 10^{-7} \exp(-E_0/kT)$$

where E_0 is the threshold energy for negative ion formation. Finally we have

$$y_i = 10^{-10}(N_i/R^{1/2}) \exp(-E_0/kT) \tag{12}$$

This formula makes clear that the fate of the electrons depends upon the rate of irradiation. For a low enough rate one expects neutral molecule capture regardless of threshold energy. It should be noted that this result applies to any case where the walls may be neglected.

If we set $y_i = 1$ we get a condition on the three values E_0, N_i and R. For a given value of E_0 and R, the corresponding value of N_i is too small to capture the electrons in competition with the positive ions (note the assumption made in the use of equation (9)). For values of N_i expressed in mm. Hg we have for the pressure of species *i*

$$p_i = 3 \times 10^{-7} R^{1/2} \exp(E_0/kT) \tag{13}$$

In Table VI values of p_i for various values of E_0/kT and R are given. For any given mixture of gases it is clear that as the rate of irradiation increases, the positive ions will become more effective in electron capture processes. One should expect in cases where negative ion formation is possible to find the mechanism, ion yield, etc., for a reaction to change as the irradiation rate is changed.

TABLE VI

VALUE OF THE PARTIAL PRESSURE p_i (IN MM.) OF A NEUTRAL MOLECULE BELOW WHICH ITS THERMAL ELECTRON CAPTURE CANNOT COMPETE WITH POSITIVE ION CAPTURE. R IS EXPRESSED IN IONS CC.$^{-1}$ SEC.$^{-1}$

E_0/kT	R 10^6	10^{10}	10^{14}
0	3×10^{-4}	3×10^{-2}	3
1	8.2×10^{-4}	8.2×10^{-2}	8.2
2	2.2×10^{-3}	0.22	22
3	6.0×10^{-3}	0.60	60
4	1.6×10^{-2}	1.6	1.6×10^2
5	4.4×10^{-2}	4.4	4.4×10^2
6	0.12	12	1.2×10^3
7	0.33	33	3.3×10^3
8	0.89	89	8.9×10^3
9	2.4	2.4×10^2	2.4×10^4
10	6.6	6.6×10^2	
12	4.9	4.9×10^3	
14	2.6×10^2	3.6×10^4	
16	2.7×10^3		

For particles which ionize densely and especially in condensed systems, the fate of the electron will change as the track gets older. At first, while the charge is concentrated, capture tends to be by the ions; later, as diffusion reduces the ion concentrations, capture by neutral molecules becomes increasingly important.

5.4. Rate of Back Reaction.—The rate of the back reaction, *i. e.*, the expulsion of the captured electron

$$R_1 + R_2^- \longrightarrow R_1R_2 + e \qquad 5.4(1)$$

$$M^- \longrightarrow M + e \qquad 5.4(2)$$

will be insignificant for reaction (1) since the dissociated fragments will be present in such small concentrations. However, if the molecule is not dissociated, as in (2), it is of some interest to investigate the conditions under which the back reaction becomes important. For example, although we might concede that O_2^- ions may be formed as described in section 2.2 there may be suspicion that they may immediately lose their electrons in the reverse process, thus maintaining a negative ion concentration effectively zero. However, the situation is not at all so simple. In a steady state, the concentration of M^- is determined by the balance between all the mechanisms for its formation and destruction. Since it is formed only by the one process, electron capture, its maximum concentration is limited by the balance between its formation

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[16] J. Sayers, *Proc. Roy. Soc. (London)*, **A169**, 83 (1938).

rate and any single destruction process. A simple way to give the condition is to express the equilibrium constant for the process in the partition function form. If we note that the vibrational, rotational and translational contributions to that function are substantially the same for the molecule and for its negative ion

$$\frac{(\mathrm{M}^-)}{(\mathrm{M})(N_e)} = \frac{h^3 \exp\,(I/kT)}{(2\pi mkT)^{3/2}} \simeq 10^{-19} \exp(I/kT) \qquad (14)$$

Since (M) $\simeq 10^{19}$ for atmospheric pressure

$$(\mathrm{M}^-)/(N_e) \backsimeq \exp(I/kT) \qquad (15)$$

As one could have anticipated, the effectiveness of the negative ion mechanism for the permanent removal of electrons depends upon the electron affinity I_- of the ion. Furthermore, the value of I_- does not have to be very great before the fraction of total negative charge carried by electrons is completely negligible, since the dependence is exponential.

6. Applications to Radiation Chemistry

6.1. Electron Capture in Various Compounds. —The general considerations above have led to a very definite requirement for the formation of negative ions due to electron capture in neutral molecules: the threshold must be small for the capture process to predominate even in a pure gas. Our considerations of the electronic states of negative ions lead to the conclusion that a low threshold can result only from good electron affinity. However, it is not generally true that capture of free electrons to give negative ions is an "all or none" process characteristic of the compound studied. The irradiation intensity as well as the pressure of that compound in a gas or its concentration in a liquid (if some other substance predominates) have very important bearing. Furthermore, in condensed systems practically every possible relative concentration of positive ions can exist along an ion track at various stages of its diffusion and disappearance; under such conditions competition between positive ions and neutral molecules for the thermal electrons may favor one or the other merely as a function of the life of the track. However, it is useful to examine certain common cases for "average irradiation conditions" to see whether negative ions formed by electron capture enter importantly into the neutralization process. Table VII summarizes the results of such an examination. We have restricted this examination to cases where "all or none" statements can be made with the restrictions noted.

TABLE VII

CLASSIFICATION OF SOME COMPOUNDS WITH RESPECT TO ABILITY TO CAPTURE THERMAL ELECTRONS AT MODERATE RATE OF IRRADIATION ($R \simeq 10^{10}$ ION PAIRS CC.$^{-1}$ SEC.$^{-1}$) IN THE GASEOUS STATE

Compound	Electron capture	Compound	Electron capture
CO	No	Hydrocarbons	No
CO_2	No	Alcohols	No[b]
NH_3	No	Aldehydes	No
NO	Yes	Carboxylic acids	No[b]
N_2O	No	Ethers	No
SO_2	Yes	Alkyl chlorides	Yes[c]
H_2S	No	Alkyl bromides	Yes
H_2O[a]	No[a]	Alkyl iodides	Yes[c]
HCl	Yes		
Cl_2	No		
Br_2	Yes		
I_2	Yes		

[a] At high gas pressures water captures electrons without threshold energy. Presumably liquid water acts similarly. *Cf.* Section 6.5. [b] In the liquid state the behavior is probably analogous to that of water. [c] Based on argument given in section 6.1.

We are concerned only with those cases in radiation chemistry in which negative ion formation by thermal electrons can play a significant role. From Table VII it is evident that such cases are the exception rather than the rule for pure substances. The two types of phenomena which may occur are summarized by the reactions

$$\mathrm{RX} + e \longrightarrow \mathrm{RX}^- \qquad 6.1(1)$$

$$\mathrm{RX} + e \longrightarrow \mathrm{R} + \mathrm{X}^- \qquad 6.1(2)$$

The O_2 molecule is typical of substances which undergo negative ion formation by route (1). The requirement is that the strength of any bond involved is greater than the electron affinity of either negative ion which might be produced by rupture of such a bond.

On the other hand, reaction (2) is a case where the electron affinity of a negative ion product is greater than the strength of the bond involved in the parent molecule. Figures 3a and 3b show potential energy relationships which might be conducive to negative ion formation by capture of a thermal electron by an isolated molecule. The two cases show the effect of successively increased electron affinity of X^-. In each case thermal electron capture to give negative ions *via* reaction (2) is possible but the mechanism involves simple electron capture and dissociation of RX^- from its attractive state. As the electron affinity of X^- increases, tendency for actual crossing of the attractive states A (of the parent molecule) and B (of RX^-) decreases. In the case shown in Fig. 3b the mechanism of negative ion formation involves an electron tunneling process the probability of which is determined by the closeness of approach of the two attractive curves A and B. We are not prepared to explain any case of negative ion formation *via* reaction (2) unequivocally on the basis of one of these cases.

When reaction (1) is the process by which negative ion formation occurs, that formation is not necessarily reflected in any effect on the ion pair yield. Various possibilities exist.

(a) The neutralization process does not involve a chemical change of the negative ion

$$\mathrm{RX}^+ + \mathrm{RX}^- \longrightarrow \mathrm{RX}^* + \mathrm{RX} \qquad 6.1(1a)$$

What happens to RX^* depends on its state of excitation. If RX^* is formed from RX^+ by electron capture, it is in the highest state of interest to us (*cf.* reference 3). The greater the electron affinity of RX^- the lower will be the state of RX^* formed *via* reaction (1a). We may expect that the nature and probability of reactions such as

$$\mathrm{RX}^* \left[\begin{array}{l} \longrightarrow \mathrm{R} + \mathrm{X}^*, \\ \longrightarrow \mathrm{R}^* + \mathrm{X}, \text{ or} \\ \longrightarrow \mathrm{R} + \mathrm{X} \end{array} \right. \qquad 6.1(1a')$$

will be greatly modified by the degree of excitation

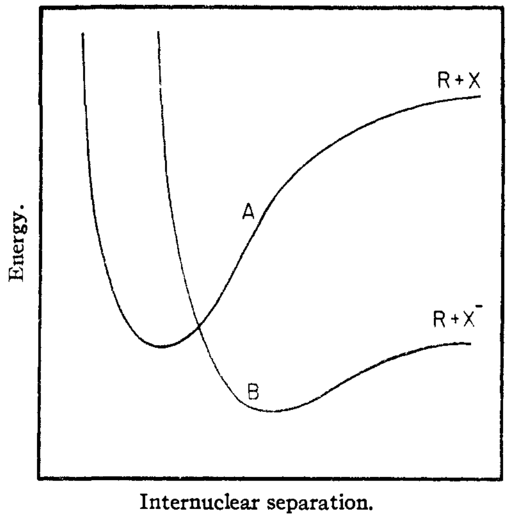

Fig. 3a.

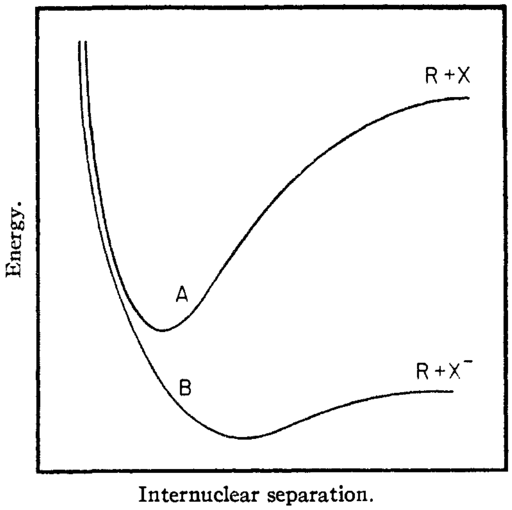

Fig. 3b.

Two possibilities for the lowest negative ion potential curves of a molecule RX.

of RX*. In general, we are inclined to conclude that the ion-pair yield of product will be less when RX* is formed by ion neutralization as in reaction (1a) than when it is formed by capture of the electron by the positive ion itself.

(b) A particularly interesting possibility ensuant on reaction (1) is the reaction

$$RX^+ + RX^- \longrightarrow R_2 + X_2 \qquad 6.1(1b)$$

or some variant on that theme. In this case formation of negative ions and their behavior in a secondary process have doubled the ion pair yield of reactant altered by the irradiation.

(c) A third possibility ensuant on reaction (1) occurs in those cases where the species RX exists as an impurity (or a second component) in a phase which is largely AB. In such case it may happen (as we later show) that the positive ions present are largely AB^+. The discharge reaction of RX^- may then be represented schematically by the reaction

$$AB^+ + RX^- \longrightarrow \text{products} \qquad 6.1(1c)$$

In contrast with compounds which form negative ions by reaction (1), those which capture thermal electrons in a dissociation process such as (2) should show an ion pair yield greater than that of substances for which the important primary reactions involve only positive ions. Consider the general reaction involving RX without negative ion formation.[17]

$$RX \rightsquigarrow RX^+ \qquad (I)$$
$$RX^+ + e \longrightarrow RX^* \qquad (II)$$
$$RX^* \longrightarrow \text{products} \qquad (III)$$

When negative ion formation occurs *via* the reaction

$$RX + e \longrightarrow R + X^- \qquad 6.1(2)$$

that step alone makes a contribution to the yield *via* the particle R. The neutralization process

$$RX^+ + X^- \longrightarrow \text{products} \qquad 6.1(3)$$

may not necessarily yield in addition to X precisely the same products as reaction (III). However, the over-all total effect is a tendency[18] to double the yield. If the products resultant from the respective neutralization processes are atoms or radicals, the ensuant reactions will depend on temperature and state. Under such conditions chain reactions may predominate and the most that can then be said is that radiation chemical reactions involving negative ions will probably show somewhat higher calculated ion-pair yields than might otherwise be expected.

6.2. Oxygen and its Reactions.—Oxygen is particularly interesting because, in addition to its excellence as a trap for thermal electrons, it also has a relatively low ionization potential, *i. e.*, not greater than 12.3 ± 0.1 ev.[19] In pure oxygen the primary effect of radiation is to produce O_2^+ ions and O_2^- ions.

$$O_2 \rightsquigarrow O_2^+ + e \qquad 6.2(1)$$
$$O_2 + e \longrightarrow O_2^- \qquad 6.2(2)$$

Neutralization of ionic charges involves both those types of ions and the ensuant important neutralization reaction might be one or more of the following

$$O_2^+ + O_2^- \begin{cases} \longrightarrow O + O_3 \\ \longrightarrow O_2^* + O_2 \\ \longrightarrow O + O^* + O_2 \\ \longrightarrow O^* + O^* + O_2 \end{cases} \qquad 6.2 \begin{cases} (3a) \\ (3b) \\ (3c) \\ (3d) \end{cases}$$

in which one or more excited oxygen atoms or molecules are produced. The ozone ultimately produced may come from the first reaction or by one of the reactions postulated in photochemistry,[20] namely

$$O + O_2 + M \longrightarrow O_3 + M \qquad 6.2(4a)$$
$$O_2^* + O_2 \longrightarrow O_3 + O \qquad 6.2(4b)$$

Only about half the energy of radiation absorbed in matter goes into primary ionization. The other half is consumed in processes which yield excited

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[17] For a detailed discussion of these reactions *cf.* Magee and Burton, ref. 3.

[18] This is only a tendency. The fixed initial contribution from primary excitation processes remains unaffected by the formation of negative ions.

[19] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1947, p. 98.

[20] *Cf.* G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Elementary Reactions," Prentice-Hall, New York, N. Y., 1939, pp. 327-329.

molecules and atoms in the first instance.[21] The energy required for the lowest excitation process (the one of most probable occurrence) is, in general, considerably lower than for the first ionization process: *i.e.* ~4.9 ev. as compared with 12.3 ev. Thus, there will be ~2.5 as many O_2^* molecules primarily produced as O_2^+ ions.

$$O_2 \rightsquigarrow O_2^* \qquad 6.2(1b)$$

The old results of Lind and Bardwell[22] on the alpha-particle induced reaction in oxygen indicated a calculated ion-pair yield not greater than 1.7 but probably greater than 1. All in all, these figures are low compared to what might be expected from the reactions shown above. The ionization process and its consequences could yield at least 2 molecules of ozone. The excitation process and its consequences can yield 2.5 × 2 or 5 molecules of ozone. A maximum readily explicably ion-pair yield is therefore 7. We have consequently to explain a relatively low yield. The readiest explanation is in the light of a back reaction involving ozone, *e.g.*

$$O + O_3 \longrightarrow 2O_2$$

but perhaps there are other explanations which involve also the participation of either positive or negative ions of ozone.

In a mixture of gases radiation acts somewhat haphazardly on all the molecules present. Not all the ions initially present long endure. As is known from studies of ionic mobility in rare gases, ions of higher ionization potential quickly transfer their charge to particles of lower ionization potential, even when the latter are present in the trace concentrations characteristic of impurities. Oxygen is a substance of characteristically low ionization potential (12.3 ev.) compared with 15.427 ev. for hydrogen,[23] 14.1 ev. for carbon monoxide,[24] and 14.5 ev. for methane.[24] In mixtures of those gases with oxygen, irrespective of the ions originally present, the only ones which can enter in any reasonable degree into the neutralization step might seem to be O_2^+ and O_2^-.

The circumstances detailed in the last paragraph, as well as in the discussion of the behavior of pure oxygen, may help to explain the curious observations of Lind and his co-workers[22b] regarding the ion-pair yield of radiation-induced oxidation of hydrogen, carbon monoxide and methane. All show remarkable constancy (*i.e.* within a factor of 2) in ion-pair yield irrespective of reactant ratios, temperature and pressure. Such constancy would not be expected on the basis of ordinary kinetic considerations. The case of hydrogen and oxygen is, moreover, genuinely startling. Over a range of temperature from −75 to +25°, over a wide range of reactant ratios and of gas pressures, the calculated ion-pair yield of water varies only in the range 3.4 to 4.0.[21]

A detailed explanation of these results cannot be attempted here. However, it is evident that the only important neutralization process in any of these systems, at any temperature, pressure or ratio of reactants is the one between the predominant positive ion species and O_2^-. The primary products of this reaction enter into the subsequent reactions, presumably with the other reactant present, at a rate which is hardly affected by temperature, for the yield is reduced but moderately in hydrogen at −75° (and only by a factor of 2 in carbon monoxide at liquid air temperature). The activation energy of the significant rate-controlling processes must be close to zero. The problem reduces to one of finding such reactions which, together with those initiated by primarily excited molecules, can give approximately the required ion-pair yield. The major importance of the neutralization process involving O_2^- accounts for the relative constancy of ion-pair yields; what variation in yields is observed is perhaps to be attributed to the contribution of the primary excitation. However, in view of the known importance[7] of the reaction

$$H_2^+ + H_2 \longrightarrow H + H_3^+$$

it is evident that the details of this reaction require very careful consideration.

6.3. Reactions of Type $A^+ + B^-$.—Imagine a system consisting of molecules A and B, in which the ionization potential of A is less than that of B and in which only B captures thermal electrons under the irradiation conditions. In such a system B^+ primarily formed by the radiation transfers its charge to A molecules. The only important neutralization process involves $A^+ + B^-$ and special reactions characteristic of such neutralization might occur.

A particularly interesting class of substances which give positive ions at low ionization potential is the aromatic group of hydrocarbons. The appearance potential[24] for the $C_6H_6^+$ ion is quoted as 9.8 ev. compared with 12.3 ev. for the ionization potential of O_2[19] (*cf.* 9.5 ev. for the appearance potential of NO^+[24]). Furthermore, benzene and its derivatives are notoriously resistant to the effects of ionizing, as well as ordinary ultraviolet, radiations. It would appear profitable to examine the possibility that such resistant compounds would nevertheless be susceptible to radiation when a suitable additional reactant such as oxygen is present. Another particularly intriguing substance which might function in this way is nitrogen dioxide. We have performed no calculations and have no other information on this point but it may be pointed out that NO_2 is an odd-electron molecule and has a low-lying vacant orbital available for entrapment of thermal electrons and that the appearance potential of NO_2^+ is 11.0 ev.

The ion B^- may be formed also by a dissociation process. For example, methyl chloride (with appearance potential[24] of CH_3Cl^+ equal to 11.0 ev.) may capture a thermal electron in a dissociation process. In this case the interaction of the Cl^- ion primarily produced with the other reactant, *e.g.*, $C_6H_6^+$, may be fruitful. The radiation chemistry of the alkyl halides as sole reactants is also interesting from this point of view, for they offer two reac-

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[21] *Cf.* M. Burton, *J. Phys. Colloid Chem.*, **51**, 786 (1947).

[22] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," 2nd Edition, Chemical Catalog Co., New York, 1929; *a*, p. 92; *b*, p. 100.

[23] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," Prentice-Hall, New York, N. Y., 1939, p. 500.

[24] Based on appearance potential data; *cf.* G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939, pp. 367 *et seq.*

tions which affect the yield and determine the nature of the products.

$$RX \rightsquigarrow RX^+ + e$$
$$RX + e \longrightarrow R + X^-$$

The reaction of X^- with RX^+ may result in reactions in which hydrogen is split out or in which the carbon chain is split into two particles each containing a halogen. Current studies by Hamill and Williams in these laboratories using radiohalogens as tracers may furnish information on these reactions.

6.4. Impurity Reactions.—Two of the most common impurities with which we have to deal in kinetics are oxygen and water. Both, as it is shown in Table VII, are effective in capture of thermal electrons. Thus, when they are present as impurities (*e.g.*, in the system M), they are particularly likely to be troublesome because the principal neutralization will no longer be

$$M^+ + e \longrightarrow M^*$$

but will involve negative ions and may, when M is of sufficiently high ionization potential, not involve M^+ at all.

6.5. Water.—In liquid water the important primary reactions are

$$H_2O \rightsquigarrow H_2O^+ + e \qquad 6.5(1)$$
$$H_2O^+ + aq. \longrightarrow H_3O^+ + OH \qquad 6.5(2)$$

and

$$H_2O,\ aq. + e \longrightarrow H + OH^-,\ aq. \qquad 6.5(3)$$

The latter reaction is of special interest for this paper. As we see from Table VII, the isolated water molecule cannot capture an electron, for the H–OH bond strength most probably exceeds the electron affinity of the isolated OH^- ion. In water vapor at high pressure, just as in liquid water, solvation becomes important. The electron affinity of the solvated OH^- ion is very high. Reaction 6.5 (3) is very exothermic and the potential energy curves are perhaps to be represented by Fig. 4. The reaction corresponds to 6.1(2). Ultimately the H_3O^+ and OH^-,aq. ions produced some distance from each other diffuse together and combine. The average H^+ and OH^- concentration throughout the solution is not significantly affected by these phenomena (except insofar as H_2O_2 produced in the radiolysis may affect the *p*H) but as Professor James Franck has recently pointed out to us (private communication) local high concentrations of either H^+ or OH^- ions produced by irradiation of aqueous systems may have profound consequences in biological material. Living material is extremely sensitive to *p*H and may suffer serious changes before diffusion can moderate local acute ion concentrations.

NOTRE DAME, INDIANA RECEIVED JULY 20, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Studies in Photochemistry and Radiation Chemistry of Toluene, Mesitylene and Ethylbenzene[1,2,3]

BY ROBERT R. HENTZ[4] AND MILTON BURTON

Toluene, mesitylene and ethylbenzene are similar to benzene in their resistance to photochemical and radiation chemical destruction. Light absorbed in the 2537 A. region, presumably by the π-electron system, produces gas non-condensable at $-120°$ with a quantum yield of the order of 10^{-4}. Quantum yields of molecules converted to polymer are roughly 16 times greater. The major primary photolysis occurs in bonds β to the ring with an additional small contribution from C–C bonds α to the ring. Atoms and radicals formed may add to a benzene ring, acquire a hydrogen atom from a methyl group in a molecule, or combine. Liquid state photolyses show considerable suppression of methane formation. Mercury-photosensitized decomposition of toluene and mesitylene gives low yields of hydrogen. In 1.8 mev. electron-induced radiolysis, 100 ev. yields of non-condensable gas range from 0.14 for toluene to 0.26 for mesitylene; *i.e.*, about 100 times greater than might be expected on a mere energetic basis by comparison with quantum yields. Radiolysis results are interpreted on the basis of energy absorption in either the ring or the side group, flow of energy from one to the other, and ensuant decomposition, the energy-yield of the latter being decreased by fluorescence from the π-electron system of the ring.

Studies of effects of high-energy electron irradiation have shown that aromatic hydrocarbons are markedly more resistant to decomposition than are other hydrocarbons.[5,6] In this work toluene, mesitylene, and ethylbenzene were chosen for study in the hope that differences in number and location of methyl groups and hydrogen atoms in the parent molecules would make possible some interpretation of the mechanism of their decomposition.

Analysis of the phenomena of radiation chemistry is complicated in part by the fact that two primary physical reactions are involved: excitation and ionization.[7] Detailed knowledge of the primarily excited states is presently lacking. Although it is usually said that they are essentially like those which may be excited by absorption of ultraviolet light, the fact is that electron bombardment may cause transitions forbidden in photon excitation. Nevertheless, the states obtained by electron bombardment probably behave similarly to those obtained in ordinary photochemistry, when due allowance is made, of course, for restrictions set up by selection rules governing transitions from those exceptional states which are not involved in photochemical processes.

Among pure aromatic compounds, benzene alone

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(1) Paper presented before Division of Physical and Inorganic Chemistry, American Chemical Society, Chicago, September 5, 1950.

(2) Abstract of a thesis submitted by Robert R. Hentz to the Department of Chemistry of the University of Notre Dame in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) The Van de Graaff generator of the Chemistry Division, Argonne National Laboratory, was employed for some of the exposures described in this paper.

(4) Recipient of fellowships from Sinclair Refining Co. and E. I. du Pont de Nemours & Co.

(5) E. G. Linder and A. P. Davis, *J. Phys. Chem.*, **35**, 3649 (1931); C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931).

(6) M. Burton, *J. Phys. Colloid Chem.*, **52**, 564 (1948).

(7) *Cf.* M. Burton, *ibid.*, **51**, 611 (1947); *Ann. Rev. Phys. Chem.*, **I**, 113 (1950).