molecule of nitrous acid" is accordingly nonexistent.

TABLE V

EFFECT OF TEMPERATURE[a]

Temperature, °C.	k_r, sec.$^{-1}$ mole^{-1} liter × 10^{-4}
20.0	1.91
25.0	2.91
30.0	4.20
34.8	6.26
35.0	6.46

[a] Ionic strength 1.00.

The dependence of the rate upon pH can be compared with the family of theoretical curves in Fig. 4 of ref. 3, which apply to methylamine as well as ammonia. The experimental data (Fig. 3) are in agreement with the theoretical curve for $Z = +1$. The activated complex for the reaction therefore carries a +1 charge, and has the formula of the nitrosomethylammonium ion $CH_3NH_2NO^+$ or a hydrated form thereof. We can write the rate law in the form

$$d(N_2)/dt = k_r(CH_3NH_3^+)(HNO_2) \quad (1)$$

though the reaction mechanism probably involves not the methylammonium ion and molecular nitrous acid, but the nitrosyl ion and molecular methylamine

$$H^+ + HNO_2 = H_2O + NO^+ \text{ (rapid)} \quad (2)$$

$$CH_3NH_3^+ = H^+ + CH_3NH_2 \text{ (rapid)} \quad (3)$$

$$NO^+ + CH_3NH_2 \longrightarrow CH_3NH_2NO^+ \text{ (rate determining)} \quad (4)$$

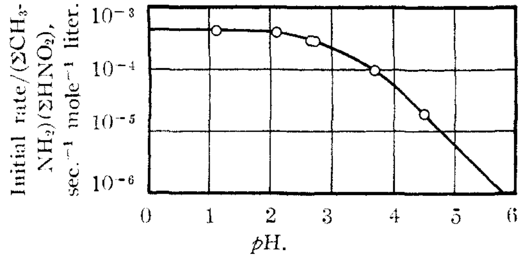

Fig. 3.—Dependence of the rate on acidity. The curve is the theoretical curve for $Z = +1$.

The rate of the reaction is the same in 0.25, 0.50 or 0.75 M phosphate buffer. The reaction shows a small negative salt effect (Table IV), which is probably caused by the effect of ionic strength on the ionization of nitrous acid.

The rate data in the temperature range 20 to 35° (Table V) are reproduced by the equation

$$k_r = (kT/h)e^{-27.8/R}\, e^{-14,000/RT} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ liter} \quad (5)$$

We wish to acknowledge the assistance of Mr. Dale Gross with the experiments reported here.

BERKELEY, CALIF. RECEIVED JANUARY 15, 1951

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

Theory of Radiation Chemistry. I. Some Effects of Variation in Ionization Density[1,2]

BY JOHN L. MAGEE

The ionization density in a homogeneous medium exposed to steady irradiation is a function of space and time. The space–time ionization density pattern depends on both the ionization density of the particles used in the irradiation and also the number of particles incident per unit time and area (*i.e.*, the rate of irradiation). In this paper a simple model is presented which describes the life of a particle track in the steady-state condition and thus also gives a description of the variations in ionization density. The author believes that this model contains the essentials of the actual physical situation, and it has the particular advantage that mathematical treatment can be carried out rigorously. In the model account is taken of the background ionization density which is present when a track is formed; this background ionization density can be higher or lower than that of the track itself depending upon the diffusion rate of the ions and radicals formed, their recombination rate constants and the rate of irradiation. Yields in radiation chemistry depend upon whether the background is high or low; this situation is discussed in terms of the model with application to some problems of radiation chemistry.

Introduction

A system exposed to a steady irradiation of charged particles has an ionization density which varies in both space and time. High concentrations of ions are produced locally with each track; at any time there will be randomly spaced tracks of various ages, and at any point in space there will be a time variation of ionization density as various tracks cross the point. The space-time pattern of ionization density, therefore, depends on both the density of ionization in the particle tracks and also upon the number of tracks per unit time falling in a region. In this paper there is reported a study of the ionization density pattern of steady state irradiations. This initial study is essentially physical and mathematical but the ultimate objective is to make application of the results to radiation chemistry, and it is hoped that progress will soon be made in this effort.

Most theoretical considerations of mechanism in radiation chemistry have essentially paralleled treatments long customary in photochemistry, and the assumption usually exists that all intermediates are created homogeneously in space. Special effects of charged particle "tracks" have been ignored. The much-quoted theory of Eyring, Hirschfelder and Taylor,[3] for example, employs this technique. We do not mean to deprecate the theoretical work in radiation chemistry, and particularly this pioneering effort of EHT,[3] but we would like to emphasize that eventually the chemical theories must recognize that the effect of a charged particle is localized in a "track." Experimentalists have for a long time recognized that there are char-

---

[1] Paper presented at Symposium on Chemistry and Physics of Radiation Dosimetry at the Army Chemical Center, Maryland, September 18, 1950.

[2] A contribution from the Radiation Chemistry Project operated by the University of Notre Dame Chemistry Department under Atomic Energy Commission Contract AT(11-1)-38.

[3] Eyring, Hirschfelder and Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

acteristic effects due to differences of ionization density along the tracks of various particles.

Several investigations of the behavior of ionization density in a particle track have been made. Jaffe[4] studied theoretically the diffusion and recombination of ions in a track to understand the efficiency of ionization chambers in counting radioactive disintegrations, Lea, *et al.*,[5,6] have considered the structure of particle tracks with regard to their physical and biological effects. It has long been recognized that biological effects depend upon the ionization density along the particle tracks. Experimental studies on the size and structure of tracks in gases are also available.[7,8]

Qualitative Description of Ionization Density Effects

Ionization produced by high energy charged particles is due partly to the direct action of the incident particle and partly to the action of the secondary electrons. The positive ions produced by the incident particle, if it is heavy such as a proton or α particle, are formed essentially along a straight line. The secondary electrons extend the region of ionization very quickly into a region of space roughly cylindrical. The time required for all the ionization in a given track to occur is very short compared with the later occurring events which are of primary interest here, and in this paper we shall assume the formation to be instantaneous. In many media of interest the electrons will be captured to form negative molecular ions. Various numbers of radicals and atoms will be formed by dissociation processes following ionization and electron capture. The spatial distribution of all their species will be essentially the same immediately after formation of a track; in certain cases there may be a small superimposed anisotropy which can be important but we shall not consider this effect here. The structure of the tracks of particles has been discussed at some length by Lea and others.[4,5,6]

The question arises as to the possible effect of ionization density on radiation chemical yields. Any product which is formed in a bimolecular reaction between an intermediate (radical or ion) and a component of the substrate must have a yield necessarily dependent upon the ionization density. The substrate competes with the recombination reaction for the intermediates; since one reaction is first order and the other is bimolecular in the intermediate, their relative rates change with ionization density. Another case, in which the product of interest is formed with definite probability on each neutralization (or radical recombination), will not have a yield which depends upon ionization density. This is clear because each ion formed must be neutralized and the product formation does not depend upon the *rate* of neutralization.

Ionization densities are varied in a number of ways. For a given medium the density along a particle track will depend upon the type of particle and its energy.[9] Steady state ionization densities will also depend upon rate of irradiation. For a given particle and energy the ionization density will depend upon the medium; the principal effect is determined, of course, by the density of the medium.

Model for Space and Time Variations of Ionization Density

In order to get a good over-all description of ionization density effects with semi-quantitative ideas of the magnitudes of the variables we construct a model which can be treated mathematically. One important object of the work reported here is to find the most significant parameters in which to express ionization density effects.

Jaffe[4] has discussed a particular model based upon a rigorous treatment of the diffusion combined with an approximate treatment of recombination. His model applies only to what we call the "low-background" case (see below). The model which we describe below was chosen because it would appear to correspond, at least roughly, to the actual physical situation and the mathematical treatment can be carried out exactly.

a. Description of Model and Fundamental Equation.—Consider a region in which parallel tracks are formed due to the incidence of particles from one direction (*i.e.*, a plane wave) at a rate ν particles per unit time per unit area. A particular track will fall into a region in which diffusion has essentially smoothed the effects of previous tracks and so we say that the background concentration is uniform with y ions of each sign per unit volume. A track formed in this region gives a higher ion concentration in a small volume which we shall call $v_0 = \pi b^2$ (since the length of track is taken as unity). The number of ions added by the track per unit length we shall call w_0. The instant the track is formed there are, in the small volume, a number of ions equal to

$$N_0 = w_0 + yv_0 \qquad (1)$$

or a local concentration of approximately

$$\frac{N_0}{v_0} = \frac{w_0}{v_0} + y \qquad (2)$$

This concentration decreases with time for two reasons: (a) the volume containing the excess ions increases by diffusion and (b) recombination occurs. The essential feature of our model is the way in which we treat the diffusion problem: we say that the volume containing the excess ions increases *linearly* with time, *i.e.*

$$v = v_0 + Dt \qquad (3)$$

We shall not attempt to justify the use of this approximation any more than to point out that it is essentially the same result as obtained by a rigorous solution of the diffusion equation for the case in which no recombination is involved. The constant D depends upon the ion or radical which is being considered and also upon the medium; apart from a factor of the order of unity, D is the ordinary diffusion constant.

The most convenient way to describe the aging of a track is to give the number of ions contained within the volume v of the track. The rate at which N changes is given by a simple differential equation

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -k\frac{N^2}{v^2}v + y\frac{\mathrm{d}v}{\mathrm{d}t} \qquad (4)$$

The first term is due to recombination and the second term to the diffusion. With the use of assumption (3) the time can be eliminated and we get

$$\frac{\mathrm{d}N}{\mathrm{d}v} = -\frac{kN^2}{Dv} + y \qquad (5)$$

The instantaneous background concentration, y, changes also, due to recombination

$$\frac{\mathrm{d}y}{\mathrm{d}t} = D\frac{\mathrm{d}y}{\mathrm{d}v} = -ky^2 \qquad (6)$$

---

(4) Jaffe, *Ann. Phys. Leipzig*, **42**, 303 (1913).

(5) Kara-Michailova and Lea, *Proc. Camb. Phil. Soc.*, **36**, 101 (1940).

(6) Lea "Action of Radiations on Living Cells," Cambridge, 1947.

(7) Klemperer, *Z. Physik*, **45**, 225 (1927).

(8) Pollermann, *ibid.*, **126**, 271 (1947).

(9) One must note that any given particle will have a varying ionization density along its track as it loses energy and slows down.

Equation 6 has the solution

$$y = \frac{y_0}{1 + \frac{k}{D} y_0(v - v_0)} \tag{7}$$

where y_0 is the concentration in the region at the instant the track is formed.

The fundamental equation of our model can now be written explicitly in the two variables N and v.

$$\frac{\mathrm{d}N}{\mathrm{d}v} = -\frac{kN^2}{Dv} + \frac{y_0}{1 + \frac{k}{D} y_0(v - v_0)} \tag{8}$$

b. Boundary Conditions.—According to the model we have a constant (in space) background concentration y_0 of ions at the initial instant of time. The number of ions is increased by the track at $t = 0$ by the number w_0. As v gets larger the concentration falls again, until at a later time when the volume of the track has grown to v_m, its largest value, the concentration has fallen to y_0. At this time, the next track must be formed if a steady condition is to be maintained, as we have assumed. During the cycle just described a total of w_0 ions have been lost by recombination: since a steady state obtains, as many ions must be lost as are added by a track during each cycle.

For $v = v_m$, we must have

$$N_m = y_0 v_m \tag{9}$$

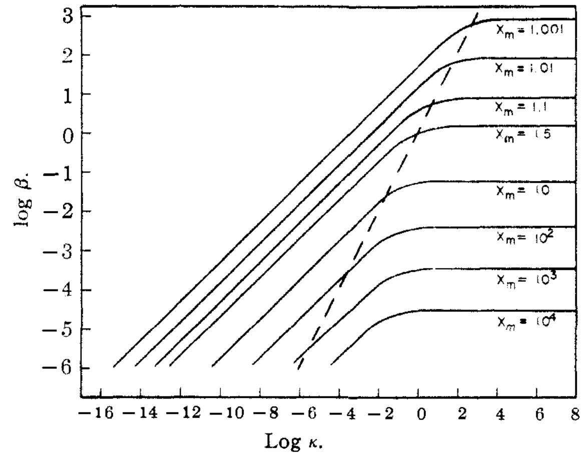

Fig. 1.—Relations among parameters required by differential equations and boundary conditions. The values of x_m at the right are constants for the solid curves. The broken line is for $\beta = \kappa$.

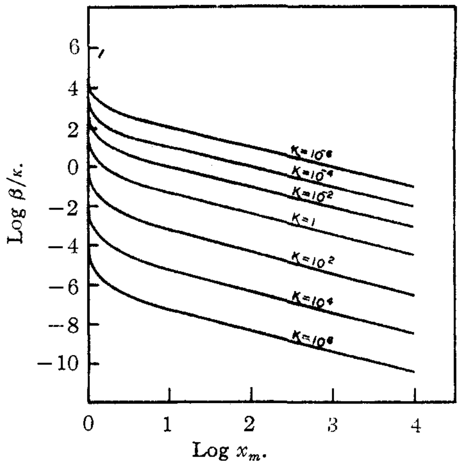

Fig. 2.—Replot of data of Fig. 1. Indicated values of κ are constants along the solid curves.

There is also a condition on the rate of irradiation set by the value of v_m. If ν is the number of tracks formed per unit area, we must have

$$\nu v_m t_m = 1 \tag{10}$$

and with the use of equation 3

$$\frac{\nu}{D} v_m(v_m - v_0) = 1 \tag{11}$$

At this point it becomes apparent that our model has eliminated the *randomness* of irradiation and substituted tracks falling at constant intervals which always expand to the same distance before the next track falls. We believe that the principal effects are obtained in this model which uses only the *average* track. Fluctuation phenomena are being investigated and will be discussed in a future publication.

c. Relations Among Parameters.—The parameters which have been introduced above as characterizing a steady state irradiation are:

ν, number of tracks per unit time per unit area
w_0, number of ions added per unit length of track
y_0, background concentration at time track is formed
k, recombination rate constant
D, diffusion parameter
$\pi b^2 = v_0$, volume of track initially
v_m, volume of track as next track hits region

The relations among these parameters are determined by the differential equation 8 together with the boundary conditions.[10] Two combinations of these parameters always appear together and so we introduce them as secondary parameters.

$$\kappa = \frac{kw_0}{D}$$
$$\beta = \frac{k}{D} y_0 v_0 \tag{12}$$

We also find it convenient to use $x = v/v_0$ as the independent variable; the largest value of x, called x_m, is the expansion ratio of the track death and we can write equation 11.

$$x_m(x_m - 1) = \frac{D}{v_0^2 \nu} \tag{13}$$

Figures 1 and 2 demonstrate the relations obtained among κ, β and x_m. All conditions for a steady state irradiation are determined if values of these three parameters are given. These figures are discussed in the next section.

Discussion

a. The High and Low Background Regions.—The most straightforward mathematical treatment of equation 8 yields results in the form given in Fig. 1.[10] Each solid line represents a solution for a certain number of tracks per unit area per unit time as indicated by the constant values of x_m at the right of the figure. The ratio β/κ at any point, as seen from relations 12, gives the ratio of the number of ion pairs (or radicals) in the initial track volume to the number introduced by the track. Thus if β/κ is large, it means that recombination is slow compared with diffusion and that at the steady state all ionization density is essentially uniform in space and time: one has a case in radiation chemistry similar to the standard photochemical case. We shall call this the "high background" case. If β/κ is small, diffusion is very slow compared with recombination and essentially all ions are lost while the track is still young: this is a case peculiar to radiation chemistry and all effects are

---

[10] This differential equation can be solved in closed form. For a brief mathematical treatment order Document 3217 from American Documentation Institute, 1719 N. St., N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

determined in isolated particle tracks. We shall call this the "low background" case.

The broken line in Fig. 1 marks the region $\beta/\kappa = 1$. To the left is the "high background" region and the right is the "low background" region. For a given medium variation along the solid lines of Fig. 1 is effected by changing the number of ion pairs per unit path of the particle; this variation can therefore be made only by changing the character of the ionizing particle. A more convenient independent variable is x_m, which is determined, for a given medium and type of particle, by the rate of irradiation. We have replotted the results in Fig. 2 as log β/κ *vs.* x_m for various constant values of κ. In this figure the horizontal line log $\beta/\kappa = 0$ separates the high and low background cases.

b. Two Cases of Interest: Water and Gas at Atmospheric Pressure.—Although x_m is a convenient parameter to employ as an independent variable, it has not been in common use and so we introduce the number of ion pairs produced per unit volume per unit time, R. From the definitions of the various quantities we must have

$$R = \nu w_0 \tag{14}$$

With the substitution of this relation in equation 13 we have

$$R = \frac{Dw_0}{v_0^2 x_m(x_m - 1)} = \frac{D^2\kappa}{kv_0^2 x_m(x_m - 1)} \tag{15}$$

In water, $R = 2 \times 10^{12}$ corresponds to one rep (roentgen equivalent physical) per second.

For illustrative purposes we choose a set of constants which should apply approximately to the behavior of H and OH radicals in irradiated water(11): $D = 8 \times 10^{-5}, k = 4 \times 10^{-10}, v_0 = 7 \times 10^{-12}$.

There is at least one other radical HO_2 which is expected in irradiated water since oxygen is usually present. Obviously the same value of k cannot apply to all pairs of radical recombinations, and so the actual system is certainly more complicated than the simple model. This treatment is, therefore, to be considered as very approximate.

Equation 15 and Fig. 2 were used to construct Fig. 3 which applies to the H and OH radicals in water with qualifications noted. For α particles $w_0 \cong 10^7 - 10^8$ so that $\kappa \cong 50 - 500$; for β particles $w_0 \cong 10^5 - 10^6$ so that $\kappa \cong 0.5 - 5$. Figure 3 shows us, therefore, that in water and aqueous solutions for any ordinary rates of irradiation we always have the low background case, as described above, for both of these types of radiation.

Thus we find that ordinarily in water we have a situation very unlike photochemistry and it is necessary to consider particle tracks for a complete description of mechanism in radiation chemistry. Extremely high rates of radiation can bring about the high background case and it would be interesting to investigate the radiation chemistry of water in this condition.

For a gas at atmospheric density we take the constants(12): $D = 1, k = 4 \times 10^{-10}, v_0 = 10^{-5}$. Figure 4 was constructed using these values. For α particles $w_0 \cong 10^4 - 10^5$, $\kappa \cong 2.5 \times 10^{-5} - 2.5 \times 10^{-4}$; for β particles $w_0 \cong 10^2 - 10^3$, $\kappa = 2.5 \times 10^{-7} - 2.5 \times 10^{-6}$. Figure 4 shows that, depending upon the rate of irradiation, one can have either high or low background cases. One can also change from one case to the other by varying the pressure; for changes of this sort, however, the constants change and a new figure must be constructed.

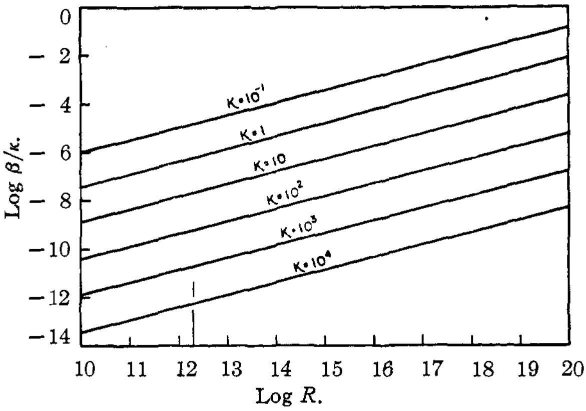

Fig. 3.—Parameter relations for radical behavior in liquid water ($D = 8 \times 10^{-5}$, $k = 4 \times 10^{-10}$, $v_0 = 7 \times 10^{-12}$). The vertical line at log R = 12.3 marks the rate of irradiation equal to one rep (roentgen equivalent physical) per second.

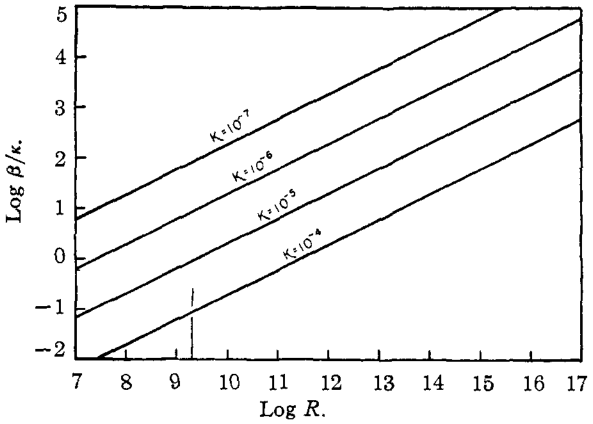

Fig. 4.—Parameter relations for radical behavior in gas at atmospheric density ($D = 1$, $k = 4 \times 10^{-10}$, $v_0 = 10^{-5}$). The vertical line at log R = 9.3 marks the rate of irradiation equal to one rep per second.

The rate constant for the recombination of ions is much larger than that for radicals. For ions formed in air Sayers(13) gives $k \cong 10^{-6}$. We use the constants $D = 1, k = 10^{-6}, v_0 = 10^{-5}$, and construct Fig. 5. Here again we see that high or low background cases can be attained, depending upon the irradiation rate. As compared with Fig. 4, the curves are all displaced to the low background region since k is larger.

The behavior of ions and radicals must be completely independent after their initial formation in order for our simple model to apply to each separately. Thus if radicals are formed in the neutralization reaction one must set up a more complicated model. However, if the values of k for radical and

(11) See Lea, ref. 6, p. 51.

(12) Lea, ref. 6, p. 50, gives a value of v_0 for air. For an order of magnitude calculation we take k the same as above. The diffusion constants of most gases have the magnitude of unity and presumably the same applies to radicals.

(13) J. Sayers, *Proc. Roy. Soc.*, **A169**, 83 (1938).

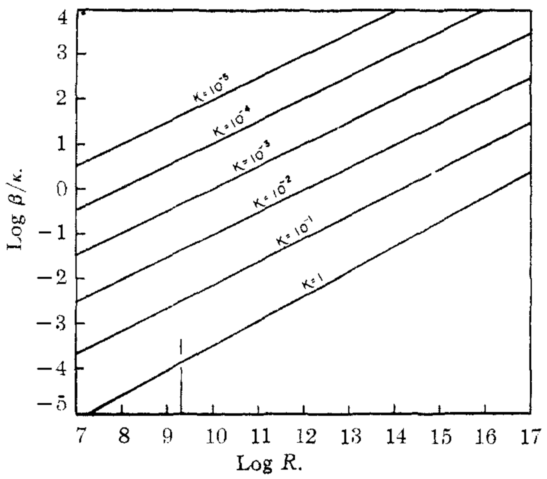

Fig. 5.—Parameter relations for ions in air ($D = 1$, $k = 10^{-6}$, $v_0 = 10^{-5}$). The vertical line marks the rate of irradiation equal to one rep per second.

ion recombination are as different as we have in this example, *i.e.*, by almost 10^4, it will be a very good approximation to treat them separately in any case. The ions recombine rapidly, before very much diffusion has taken place, and thus all radicals are formed in essentially the initial track volume. Subsequently the radicals diffuse and recombine without being influenced by ions.

c. Application to Radiation Chemistry.—The fact that the low background case always applies to liquid water and aqueous solutions furnishes certain simplifications. Without a detailed calculation it is clear that in order for a solute to compete favorably for the radicals formed by radiation, the concentration of this solute must be comparable to the initial radical concentration in the track. Thus, most effects will be correlated to the initial ionization density. An interesting example is the "back reaction" of the H_2 gas produced by radiation.[14] The steady state H_2 pressure is the order of one hundred times greater for α particle irradiations than for X-rays. The ratio is the order of the initial ionization densities in the particle tracks.

A detailed treatment must be made in which the reaction of intermediates with substrate components is considered. We can, however, give a semi-quantitative criterion for the importance of such a reaction in terms of our parameters. For low background, the initial recombination rate is

$$k(w_0/v_0)^2$$

and the initial rate of reaction with a substrate component is

$$k'(w_0/v_0)C$$

where k' is the reaction rate constant and C is the concentration of the component in question. If we have

$$kw_0 > k'v_0C$$

the recombination will dominate and relatively few of the radicals will undergo the reaction in question. If, on the other hand

$$kw_0 < k'v_0C$$

most of the radicals will react with the substrate and this reaction becomes important.

If we have the high background situation, as we have mentioned above, the considerations of ordinary photochemistry apply. Here if we are considering the reaction of an intermediate with a substrate component, the recombination is a homogeneous reaction with the rate ky_0^2 and the reaction in question has the rate $k'y_0C$. The criterion for the dominance of recombination becomes $ky_0 > k'C$ and the criterion for the importance of the reaction in question is $ky_0 < k'C$.

In the high background case the intermediate concentration y_0 varies as the *square root* of the rate of irradiation as one sees from the figures and equation 7 of the appendix. A detailed discussion of electron capture in a substrate component for this case has been made by Magee and Burton in another paper.[15]

d. Criticism of Model.—The model described in this paper gives a qualitative description of ionization density effects to be expected in radiation chemistry. The question arises as to how quantitative the model can be made in particular cases. The details of the actual processes which occur during the life of a track must be studied to answer this question. The initial spatial distribution of ions is most likely given better by a function of the distance, d from the center of the track, such as

$$n = (w_0/v_0)\exp(-d^2/b^2) \qquad (16)$$

rather than by

$$n = \frac{w_0}{v_0};\quad 0 \leqq d \leqq b \qquad (17a)$$

$$n = 0;\quad b \leqq d \leqq \infty \qquad (17b)$$

which we have taken. However, as pointed out by Jaffe,[4] it is impossible to solve the diffusion equation with recombination occurring simultaneously. The approximation adopted by Jaffe to obtain an analytical solution involves the use of a fictitious recombination coefficient which makes his result as questionable as the model adopted in this paper.

The use of the *average* track with neglect of all fluctuation effects is open to question. Since recombination makes the equations non-linear, it is expected that fluctuation effects may be appreciable in certain cases.

Tracks in many substances will have several kinds of radicals which combine in pairs and react with the substrate to form other radicals. Thus the simple model will have to be replaced by a more complicated one which carries along all radical concentrations. A set of coupled equations must be used. A feature of this model is that it can be extended to treat such cases.

The above remarks indicate that at the present time the model of this paper is most useful in a qualitative or at best semi-quantitative sense. It brings out relations between the various parameters of the problem such as ionization density along the track, rate of irradiation, recombination coefficient for ions and radicals, diffusion constant, etc. It also furnishes a guide to concentrations at which substrate components should enter reaction in irradiated systems.

There is no critical experiment or set of experi-

---

(14) Allen, *J. Phys. Chem.*, **52**, 479 (1948).

(15) Magee and Burton, THIS JOURNAL, **73**, 523 (1951).

ments to check the adequacy of this model for use in radiation chemistry. Work is now in progress to determine its usefulness in the interpretation of experimental results. Later papers of this series will present these studies.

It is known that all particles do not have an ionization density high enough to form a continuous track. The present model breaks down when the average distance between the ions formed by the primary particle exceeds the parameter b. Possibly a second simple model can be constructed to describe these cases.

The author would like to thank Professor Milton Burton and Dr. Robert R. Hentz for reading the paper in manuscript and for helpful discussions and Messrs. E. F. Gurnee and A. H. Samuel for helping with the figures.

NOTRE DAME, IND. RECEIVED NOVEMBER 22, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Action of Liquid Ammonia Solutions of Potassium and Potassium Amide upon Iron(II) Bromide[1]

BY GEORGE W. WATT AND W. A. JENKINS, JR.[2]

Treatment of iron(II) bromide with potassium in liquid ammonia at −33.5° yields an ammonia-insoluble product consisting of elemental iron, iron(I) nitride, and one or more products of the interaction of iron(II) bromide and potassium amide. The iron produced in these reactions is pyrophoric, does not contain adsorbed hydrogen, has a surface area of 8 m.^{2}/g., and is inactive as a catalyst for the hydrogenation of certain olefins at 30° and a hydrogen pressure of 2 atm.

The experiments described in this paper represent a continuation of studies on the reduction of salts of Group VIII elements to the corresponding metals by means of solutions of metals in liquid ammonia.[3] In these studies, emphasis is placed upon the properties of the reduction products, particularly with reference to their activity as hydrogenation catalysts.

Experimental

Materials.—With the exception noted below, all chemicals used in this work were reagent grade products used without further purification or were the same as those described previously.[3]

Iron(II) bromide was used in the form of the 6-ammonate which was prepared by a method that will be described elsewhere.[4]

Anal. Calcd. for $FeBr_2{\cdot}6NH_3$: Fe, 17.6; NH_3, 32.1. Found: Fe, 17.9; NH_3, 32.2.

Experimental Methods.—Unless otherwise specified, equipment and techniques employed were the same as those described earlier.[3] Reactions involving ammonia solutions of potassium were carried out in an apparatus of the type described by Watt and Moore[5]; those employing ammonia solutions of potassium amide were effected in equipment described by Watt and Keenan.[6] Electron photomicrographs were obtained using an RCA Type EMU-1 electron microscope; samples in Parlodion film were mounted on 200 mesh screen.[7]

The Reaction between Iron(II) Bromide and Potassium.—In a typical case, 2.932 g. of iron(II) bromide 6-ammonate suspended in 25–30 ml. of anhydrous liquid ammonia was treated with 1.209 g. of potassium ($K/FeBr_2$ = 3.35) added in one portion. All of the potassium reacted within 10 sec., hydrogen evolution was continuous throughout the total reaction time, and the bromide was converted to a black finely divided solid. The pale yellow supernatant solution was removed, the solid washed five times with 25-ml. portions of ammonia, resuspended in 25–30 ml. of ammonia, and treated with an additional 0.598 g. of potassium ($K/FeBr_2$ = 1.66). Again, hydrogen evolution was continuous, but there was no visual evidence of change in the solid phase. The ammonia-insoluble solid was washed with liquid ammonia until the washings were free of bromide ion and thereafter dried for 20 hr. at room temperature and a pressure of 0.1 mm. The resulting black solid was highly pyrophoric; qualitative tests for bromide ion were negative. Data relative to these reactions are given in Table I; variation in reaction ratios and mode of addition of potassium failed to alter appreciably the composition of the ammonia-insoluble products.

TABLE I

REDUCTION OF IRON(II) BROMIDE WITH POTASSIUM

$FeBr_2{\cdot}6NH_3$, g.	K, g.	$K/FeBr_2$	H_2, cc.	Insoluble product Fe, %	N, %
2.264	0.656[a]	2.36	83.7	76.6	6.2
2.932[b]	1.209	3.35	225.6		
	0.598	1.66	121.6	80.6	5.7
3.020	.846	2.28	106.4		
	.848	2.28	209.4	80.5	5.0
3.117[c]	.862	2.21	108.0		
	.947	2.47	211.9	82.3	7.1
2.243[d]	.875[a]	3.40	153.0	84.6	3.6

[a] One addition of potassium. [b] The insoluble product was analyzed for potassium. Found: 9.7%; total accounted for, 96.0%. [c] Potassium content of insoluble product, 6.5%; total accounted for, 95.9%. [d] Initial volume was 12–15 ml. rather than 25–30 ml.

The Reaction between Iron(II) Bromide and Potassium Amide.—In the course of efforts to identify products formed in the reduction of iron(II) bromide with potassium, the reaction between this salt and potassium amide was studied. A suspension of 2.702 g. of iron(II) bromide 6-ammonate in 50 ml. of ammonia was treated with 10 ml. of ammonia solution containing the potassium amide equivalent to 0.719 g. of potassium. The bromide was immediately and completely converted to a black insoluble solid which was washed and dried as described above. This product also was markedly pyrophoric.

Anal. Found: Fe, 61.0; N, 15.9; K, 8.7.

Preparation of Potassium Amide.—In order to obtain samples for X-ray diffraction patterns, potassium amide was prepared by the iron-catalyzed interaction of potassium and liquid ammonia.

Anal. Calcd. for KNH_2: K, 70.5. Found: K, 69.9.

X-Ray Diffraction Patterns.—As a means of identifying the products of the reduction of iron(II) bromide, X-ray

---

[1] This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

[2] Radiation Laboratory, The University of California, Berkeley, California.

[3] G. W. Watt, W. F. Roper and S. G. Parker, THIS JOURNAL, forthcoming publication.

[4] G. W. Watt and W. A. Jenkins, Jr., "Inorganic Syntheses," Vol. IV.

[5] G. W. Watt and T. E. Moore, THIS JOURNAL, **70**, 1197 (1948).

[6] G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

[7] The assistance of Mr. L. L. Antes is gratefully acknowledged.