252. *The Non-homogeneous Reactions following Neutron Capture in Organic Bromides.*

By MIRIAM MILMAN and P. F. D. SHAW.

An attempt is made to treat quantitatively the kinetics of the reactions occurring between radicals and inorganic radio-bromine compounds formed near the site of neutron capture. Allowance for the dilution of the reactants by diffusion has been made by considering these to be held uniformly in a sphere of liquid whose radius increases with time. By making reasonable assumptions regarding the rates of the reactions involved, curves have been obtained which fit the experimentally determined variation of retention with bromine concentration in ethyl bromide, ethylene dibromide, and tri- and tetra-bromoethane.

THE sharp fall in retention which is observed when small quantities of elementary bromine are added to organic bromides before neutron irradiation has been ascribed [1, 2] to thermal processes involving diffusion of the radicals produced by the recoil atom. The preceding papers [3,4,5] support this view, and also provide evidence for the nature of such diffusive reactions.

The basic difficulty in a quantitative treatment of the kinetics of such reactions, where some of the reactants are not homogeneously distributed, is to allow for diffusion. The general equation describing such processes is

$$dc/dt = D\nabla^2 c - k_c c^2 - k_s c s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

---

[1] Goldhaber and Willard, *J. Amer. Chem. Soc.*, 1952, **74**, 318.
[2] Roy, Williams, and Hamill, *ibid.*, 1954, **76**, 3274.
[3] Milman and Shaw, *J.*, 1957, **1303**.
[4] Milman, Shaw, and Simpson, *J.*, 1957, **1310**.
[5] *Idem*, preceding paper.

The first term takes account of the diffusion (coefficient $= D$), the second the recombination between radicals at concentration c, and the third represents reaction between the radicals and some other species (concentration s) which may be uniformly dispersed throughout the system.

Approximations have been made to make this equation solvable. Of these, most assume that the radical distribution is Gaussian, and remains so with time (cf., *e.g.*, Krenz [6]); in particular this assumption is inherent in the treatment by Samuel and Magee [7] which has been applied by Roy *et al.*[2] to the recombination occurring in Szilard–Chalmers reactions.

This assumption makes the mathematical handling of the equation easier; this is its only justification. There are two possible criticisms of such a treatment applied to recoil effects. The initial Gaussian distribution is expected if a cluster of non-reactive radicals started from a point and were allowed to diffuse freely through the liquid. Such distributions only hold for a large number of diffusive " jumps " (displacement from one " lattice " site in the liquid to a neighbouring one), and in the present case this approximation may not be valid. For example, if it is assumed that the mean energy of a bromine atom following neutron capture is 50 ev and that Br–Br (elastic) collisions are chiefly responsible for its slowing down, the mean time for the energy to become about 1 ev must be approximately that required to make 7 suitable collisions, since the mean fraction of the energy lost per collision is 0·5. If x is the mean distance between bromine atoms, and v_0 the initial recoil velocity, the time required to make these is $(x/v_0)\{1 + (2)^{\frac{1}{2}} + (2) + \ldots . (2)^{6/2}\}$, *i.e.*, about $25x/v_0$. Any potential barrier to diffusion being neglected, the mean time for a thermal atom to traverse x is x/v; since v_0 is 45 times greater than v it can be seen that the recoil atom is thermalised in a time which is small compared with that required for thermal atoms or radicals to move one molecular diameter. This argument is extremely crude, and neglects the increased rates of diffusion of the radicals which would be expected in view of the large energies involved, but it indicates that any large amount of diffusion such as that necessary to obtain an initial Gaussian distribution is unlikely.

The second criticism of the treatments cited is that if recombination is to be important, the concentration distribution cannot remain Gaussian since the rate of recombination is proportional to c^2 and therefore the central maximum of the latter will be depressed more rapidly with time than its periphery. Also, if the diffusive reactions are imagined to occurr after the high-energy recombinations, it seems improbable that the initial distribution of radicals will be Gaussian.

An alternative assumption which enables us to solve eqn. (i) is that the radicals produced are held at uniform concentration in a small sphere of liquid, the periphery of which expands at a rate given by the mean distance traversed in a three-dimensional random walk. A similar picture of the diffusive reactions occurring near more energetic particle tracks has been given by Magee.[8] The initial distribution of the radicals produced by recoil atoms may be reasonably well interpreted by this assumption, since the energetic atom will be widely scattered so that an approximately spherical radical distribution might result.

In a random-walk treatment, the mean displacement (r), in time t, of radicals starting from a point and diffusing in all directions is given by:

$$r^2 = (1/3)\delta^2\nu t = 2Dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where ν is the frequency at which steps of length δ (assumed subsequently to be a molecular diameter) are taken and D is the diffusion coefficient. At any time (t) after neutron capture, the volume containing the radicals, etc., is given by:

$$V(t) = (4/3)\pi[2D(t_0 + t)]^{3/2}$$

---

[6] Krenz, *J. Chim. phys.*, 1951, **48**, 237.

[7] Samuel and Magee, *J. Chem. Phys.*, 1953, **21**, 1080.

[8] Magee, *J. Chim. phys.*, 1955, **52**, 528.

where t_0 is a constant which determines the initial size of the radical cluster. The rate of combination of a group of radicals diffusing from a common origin is given by

$$-\mathrm{d}n(t)/\mathrm{d}t = k[n(t)]^2/[\rho V(t)] = k[n(t)]^2/[\alpha(t_0 + t)^{3/2}]$$

where

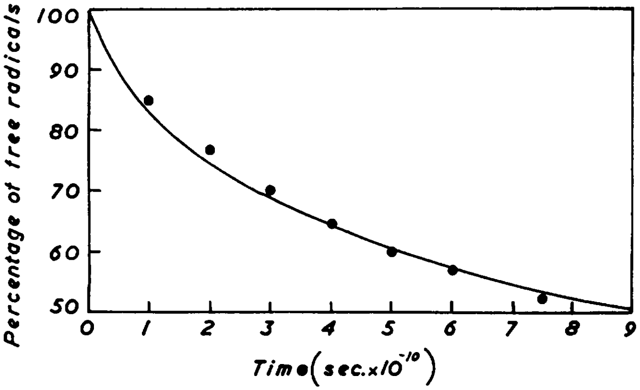
$$\alpha = 4\pi(2D)^{3/2}\rho/3$$

or

$$1/n(t) - 1/n(0) = 2(k/\alpha)\{t_0^{-\frac{1}{2}} - (t_0 + t)^{-\frac{1}{2}}\} \quad . \; . \; . \; . \; . \quad \text{(iii)}$$

where $n(t)$ is the number of radicals present at time t, ρ is the number of solvent molecules in unit volume, and k is a reaction constant equal to a collision number multiplied by the probability of recombination per collision.

This treatment of the diffusion is unrealistic, and it is of interest to compare it with some other in which it is possible to treat the diffusion more realistically. This has been performed for a radical distribution which was initially Gaussian, by calculating the recombination occurring in individual shell-like volumes round the origin. The decrease in the number of radicals was found for a period of 10^{-10} sec. and the new radical concentration in each shell was calculated. The number of radicals diffusing from one shell into its neighbour in the same time was then found from the formula



The percentage of free radicals as a function of time. The curve is for a Gaussian distribution. The points were obtained from the simple theory by adjustment of t_0.

$$\Delta n/\Delta t = DA(\partial c/\partial r)$$

where Δn is the decrease in the number of radicals enclosed in a shell having surface area A in a time Δt (10^{-10} sec.). $(\partial c/\partial r)$ is the concentration gradient determined from the slope of a constructed curve. The number of radicals reacting in the next 10^{-10} sec. interval was then determined and the process repeated several times. The curve of the number of radicals which had reacted in time t is given in the Figure and was obtained from the initial Gaussian distribution

$$c_r = c_0/\lambda^3(2\pi)^{3/2} \exp{[-(r^2/2\lambda^2)]}$$

where c_r is the concentration at a distance r from the origin.

The following values of the constants required for the construction of the curve in the Figure were chosen arbitrarily; $c_0 = 19{\cdot}3$; $\lambda = 8{\cdot}75 \times 10^{-8}$ cm.; $k = 1{\cdot}63 \times 10^{10}$/sec.; $D = 1{\cdot}16 \times 10^{-5}$ cm.^{2}/sec., and $\rho = 7{\cdot}15 \times 10^{21}$/cm.^{3}. The points shown were obtained from (iii) by using the same values of k, ρ, and D. It can be seen that, by suitable adjustment of t_0, the simplified treatment can be made to give a satisfactory description of such diffusive processes; the value of t_0 chosen was $15{\cdot}2 \times 10^{-10}$ sec. and corresponds to an initial radius of the radical cluster of 18·7 Å, a value just greater than twice the Gaussian modulus (λ).

Application to Szilard–Chalmers Reactions.—In order to apply the above treatment to Szilard–Chalmers reactions, it is convenient to take initially a simplified view of the diffusive processes. In the presence of bromine (where c now represents the molar fraction N_{Br}) the rate of disappearance of organic radicals [number $n_1(t)$] from the system at time t is given by

$$-\frac{\mathrm{d}n_1(t)}{\mathrm{d}t} = \frac{k[n_1(t)]^2}{\alpha(t_0 + t)^{3/2}} + k_2 n_1(t)c + \frac{k_3 n_1(t) n_2(t)}{\alpha(t_0 + t)^{3/2}} \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

where k_1, k_2, and k_3 are reaction constants governing recombination, reaction with (inactive) bromine, and combination with the active bromine atom respectively. $n_2(t)$ is the number of radio-bromine atoms in the " reaction " volume at time t; strictly its value can only be unity for a single recoil, and therefore it must be regarded as the mean fraction (obtained from the average of many recoil events) of such atoms existing at time t. Temporarily, let us regard the radio-bromine atom as being free, allowance being made subsequently for the possibility of its being present as molecular bromine or hydrogen bromide; further, we shall also suppose that $n_1(t) > n_2(t)$, so that the last term of (iv) can be neglected in comparison with the first, and that c remains unaltered despite the large free-radical concentration produced in the vicinity of the recoil atom.

The rate of reaction of the radio-bromine atoms to give organic retention is

$$-\mathrm{d}n_2(t)/\mathrm{d}t = k_3 n_1(t) n_2(t)/[\alpha(t_0 + t)^{3/2}] \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

The solution of these equations, which was obtained by Professor M. H. L. Pryce, is given in the Appendix and is :

$$n_2(\infty)/n_2(0) = [1 + x(1 - y)]^{-k_2/k_1} \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

where

$$x = 2k_1 n_1(0)/(\alpha t_0^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

and

$$y = \pi^{\frac{1}{2}}(k_2 c t_0)^{\frac{1}{2}} e^{k_2 c t_0} \left[1 - (2/\sqrt{\pi}) \int_0^{\sqrt{(k_2 c t_0)}} e^{-z^2} \mathrm{d}z\right] \quad . \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

The quantity $n_2(\infty)/n_2(0)$ represents the fraction of radio-bromine atoms which escapes reaction with other radicals, and therefore the quantity $[1 - n_2(\infty)/n_2(0)]$ is the fraction of the atoms which has undergone diffusive retention.

If n_2 is now re-defined to mean the number of inorganic molecules (or atoms) of any type containing the radio-bromine atom, the fraction of the collisions between these and the organic radicals which is successful in causing organic retention of the radio-bromine will be P_{R} (preceding paper) so that the overall diffusive retention $[R_{\mathrm{D}}(c)]$ becomes $P_{\mathrm{R}}[1 - n_2(\infty)/n_2(0)]$. Strictly, it may be more rigorous to multiply the right-hand term of (v) by P_{R}, and the introduction of P_{R} after finding $[n_2(\infty)/n_2(0)]$ is only justified by the greater ease of curve-fitting which results from this treatment. However, neither treatment will be exact, if, as seems probable, the distribution of the active chemical species undergoing reaction alters with time, so that P_{R} should be a function of time rather than the mean value used.

The value of P_{R} obviously depends on the bromine concentration since, when this is large, it must influence the ultimate form of the radio-bromine atom resulting from the high-energy processes. For example, it would be expected that, as the bromine concentration becomes greater, more BrBr^* might be produced at the expense of HBr^*. Since it is not possible to determine the value of P_{R} directly in such circumstances it is assumed that the expression $P_{\mathrm{R}} = 0{\cdot}30 + 0{\cdot}92 \times 10^{-3}M$ holds,[5] where M is the effective molecular weight [equal to $c \times$ (molecular weight of bromine) $+ (1 - c) \times$ (molecular weight of RBr)].

A further correction must also be introduced, since the above values of P_{R} were determined for pure organic bromides. Since the number of solvent molecules affected by the recoil will be reduced when c is increased, the number of resulting organic free radicals will be less, and hence also the total number of collisions leading to retention of the radio-bromine. To allow for this, the value of $R_D(c)$ obtained above has been multiplied by $(1 - c)$, the molar fraction of the organic bromide.

Finally, the value of $R_D(c)$ must be normalised to take account of the retention due to high-energy processes. The value of the latter is $R_E(1 - c)$, since it is known empirically[3, 4] to be a linear function of c; the fraction of the total radio-bromine available to undergo diffusive reactions is therefore $[1 - R_E(1 - c)]$.

The complete expression for $R_D(c)$ is therefore

$$R_D(c) = [1 - R_E(1 - c)](1 - c)P_R[1 - n_2(\infty)/n_2(0)] \quad . \quad . \quad . \quad \text{(ix)}$$

and that for the total retention, $R(c)$:

$$R(c) = R_E(1 - c) + R_D(c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(x)}$$

The curves drawn for the retention as a function of the molar fraction of bromine in the preceding papers were given by (x) by making the assumption that $k_3 = k_1$. The values of R_E and P_R are given in the preceding paper, the x and k_2t_0 values shown in the Table also being used. Curves of reasonable fit can also be obtained by using modified values of the ratio k_3/k_1; values of x and k_2t_0 giving reasonable agreement with the experimental data are also given in the Table for $k_3/k_1 = 0{\cdot}5$.

	Ethyl bromide		Ethylene dibromide		Tribromoethane		Tetrabromoethane	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
x	1·10	3·40	0·62	1·62	0·74	1·96	0·90	2·60
k_2t_0	23·4	34·0	8·7	11·2	34·1	39·5	36·0	41·8
10^5D (cm.^{2}/sec.)	3·0		0·67		0·32		0·15	
$10^8\delta$ (cm.)	6·2		6·5		6·9		7·2	
$10^{-10}\nu$	4·66		0·95		0·40		0·17	
$10^{10}t_0f_2$	5·0	7·3	9·15	11·7	86·1	98·5	212	246
$10^8r_0f_2^{\frac{1}{2}}$	17·3	21·0	11·1	12·6	23·4	25·2	25·2	27·2
10^8r_0 (cm.)	—	—	40·2	45·6	—	—	28·6	30·8
$n_1(0)f_1f_2^{\frac{1}{2}}$	4·05	15·1	1·32	4·05	3·36	9·55	4·31	13·5
$n_1(0)$	—	—	4·8	14·8	—	—	4·95	15·3

(*a*) for $k_3/k_1 = 1$. (*b*) for $k_3/k_1 = 0{\cdot}5$.

Interpretation of the constants given is very difficult in view of the uncertainty of the relative reaction rates (k_1, k_2, k_3) and the appropriate diffusion coefficients. Values of the latter have been given by Miller[9] for iodine in ethylene dibromide and tetrabromoethane, and are included in the Table. The value of D for ethyl bromide was estimated from the viscosity by assuming Stokes's law, and that for tribromoethane was found by interpolation between the values for the other bromides. Since the values of both x and k_2t_0 contain reaction constants, it is necessary to evaluate these before estimates of t_0 (and hence the initial size of the radical cluster) and $n_1(0)$ can be made. Let k_1, k_2, and k_3 equal νf_1, νf_2, and νf_3 respectively, where ν is the frequency of " lattice jumps " or collision sets in the liquid, and f is the reaction probability per collision set. ν can be estimated from the Einstein relation[10] $D = 1/6\nu\delta^2$ where δ is the mean displacement per " jump." By taking δ to be one molecular diameter, the values of ν given in the Table are obtained.

From the values of (k_2t_0) and ν, t_0f_2 may be found and hence also $r_0f_2^{\frac{1}{2}}$ [from (ii)]. If f_2 is a constant for all the bromides, it can be seen from the Table that the decrease of r_0 expected for the more heavily brominated compounds does not occur. This anomaly is removed by more careful consideration of f_2; the probability of reaction in a given collision set is of the form:

$$f = A_R \exp(-E_R/\boldsymbol{R}T)/[A_R \exp(-E_R/\boldsymbol{R}T) + A_D \exp(-E_D/\boldsymbol{R}T)]$$

where E_R and E_D are the activation energies required for reaction and diffusion respectively and A_R and A_D are the factors depending on the collision rate of the radical with the walls

---

[9] Miller, *Proc. Roy. Soc.*, 1924, *A*, **106**, 724.

[10] Einstein, *Ann. Physik*, 1905, **17**, 549.

of the liquid cage, etc.[11] E_D can be evaluated for ethylene dibromide and tetrabromoethane from Miller's data [9] by assuming that the dependence of D on temperature is of the form $D = D_0 \exp(-E_D/\boldsymbol{R}T)$ (cf. Frenkel [12]). The values of E_D obtained for these substances are 3·5 and 5·7 kcal./mole respectively.

E_R for the reaction :

$$\mathrm{BrCH_2{\cdot}CH_2{\cdot} + Br_2 \longrightarrow BrCH_2{\cdot}CH_2Br + Br} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

is greater [14] than 5 kcal./mole; by taking the lowest estimate of E_R, and by assuming the equality of A_R and A_D, the values of f_2 for ethylene dibromide and tetrabromoethane are 0·076 and 0·77 respectively. The values of r_0 obtained are shown in the Table, and exhibit the expected fall in moving to tetrabromoethane. Similar calculations for ethyl bromide and tribromoethane are prevented by the lack of diffusion data; however, it is reasonable to suppose that E_D increases in the series of bromides, in which case the value of r_0 for ethyl bromide might be anomalously high. This could be accounted for if the activation energy of the reaction :

$$\mathrm{C_2H_5{\cdot} + Br_2 \longrightarrow C_2H_5Br + Br{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

is lower than that of reaction (*a*). This seems probable when the data of Anderson and Van Artsdalen [13] are compared with those of Muller and Schumacher.[14]

The values of r_0 are subject to large uncertainty in view of the assumptions which are necessarily made. For ethyl bromide, the distance moved by a recoil atom should correspond to about six molecular diameters (an average of 1 Br–Br collision per molecule being assumed), *i.e.*, the value of r_0 expected should be *ca.* 18 Å. For the more heavily brominated compounds this should be less. However, enhanced diffusion owing to the effective rise in temperature of the molecules near the recoil site, or delay of a γ-ray in the cascade following neutron capture would both cause a wider spread of the radicals before recombination by diffusion could occur, and in view of this the values of r_0 do not seem unreasonable.

The remaining factor of interest is $n_1(0)$, the number of radicals initially present in the " reaction volume." This can be calculated in terms of f_1 and f_2 from (vii) by using the t_0 values already determined. It can be seen that the values of $n_1(0)/f_1f_2^{\frac{1}{2}}$ given in the Table are sensitive to changes in the value of k_3/k_1 chosen. By assuming the above values of f_2, and also that f_1 is unity for recombination reactions, the values of $n_1(0)$ for ethylene dibromide and tetrabromoethane can be calculated. The smallness of the $n_1(0)$ values (for k_3/k_1 unity) is consistent with the picture of the events following neutron capture given previously [5] since the bulk of the radicals produced will be removed in the " high-energy " recombination processes. A further factor which might also account for this is that inactive bromine or hydrogen bromide molecules, produced by the recoil, will reduce the local free-radical concentration by reactions other than the simple recombination postulated. Since no transfer of activity results from such processes, it is not possible to estimate their importance, but it might be expected that, owing to this effect, the effective number of radicals would be less than the true number present. The $n_1(0)$ values also reflect the uncertainty in f_2; comparison of the values of $n_1(0)/f_1f_2^{\frac{1}{2}}$ indicates that if the value of f_2 used for ethylene dibromide were also applied to ethyl bromide, $n_1(0)$ for the latter would be 14·5, a value considerably greater than that found for ethylene dibromide or tetrabromoethane. However, if it is assumed [12] that reaction (*b*) has zero activation energy, this anomaly is removed.

The treatment given might help to account for the equality, in a given bromide, of the retentions of the different bromine isotopes. *A priori*, these might be expected to differ, since the γ-ray cascades following neutron capture, and hence the mean recoil energies, might differ considerably for the three isotopes produced. At zero bromine concentration

---

[11] Williamson and LaMer, *J. Amer. Chem. Soc.*, 1948, **70**, 717.

[12] Frenkel, " Kinetic Theory of Liquids," Clarendon Press, 1946, p. 190.

[13] Anderson and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 479.

[14] Muller and Schumacher, *Z. phys. Chem.*, 1939, *B*, **42**, 327.

R_D is determined solely by x, y being zero; for a given bromide, x is proportional to $n_1(0)/t_0^{\frac{1}{2}}$ which corresponds to the number of radicals produced per unit length of recoil track. If the latter were constant over the range of recoil energies produced by neutron capture, values of R_D for the isotopes would be expected to be equal.

The constancy of R_E for the different isotopes cannot yet be explained in view of the lack of data concerning the γ-ray cascades following neutron capture by the bromine isotopes, and the uncertainty of the exact nature of the high-energy processes. However, it is possible to formulate the simplest assumptions, based on the conclusions of the preceding paper, which could lead to constant isotopic R_E values.

To account for the approximate constancy of R_E (obtained for any isotope) in bromides containing more than one bromine atom per molecule, it has been postulated that the high-energy products result from a system in which the thermalised atom is surrounded by a cluster of free radicals and atoms, the ratio of the numbers of these being constant. For such a state to be probable, an atom having an energy E_0 (the minimum energy to ensure the complete dissociation of the neighbouring molecules) must be rapidly degraded to thermal energies. Such thermalisation must occur without appreciable diffusion of the active atom; consequently it must be brought about by inelastic collisions rather than elastic processes involving several collisions. It therefore seems probable that the process of "inelastic" thermalisation is the same as that producing the dissociation of the surrounding molecules.

The constancy of R_E for the different isotopes can be explained if it is further assumed that the majority of the individual recoil energies for any of the bromine isotopes is greater than E_0, and also that the slowing by inelastic collisions is roughly continuous, so that a stage where the energy is reduced to E_0 is probable for all atoms. It is improbable that the value of E_0 would be less than 15 ev, but a proper estimate cannot be made owing to the lack of a theoretical basis for the inelastic slowing-down process; this need, of course, makes the whole explanation of the constancy of R_E extremely tentative.

It is interesting to compare the present results for the diffusive retentions in ethyl bromide with those obtained by Roy *et al.*[2] who have also attempted a treatment of the non-homogeneous reactions following neutron capture. These authors concluded that, in ethyl bromide, the latter could be well represented by the combination of a single radical with the active atom, the distance between these being of the order of a molecular diameter. In the present treatment, the value of $n_1(0)/r_0$ required to give a retention of 32% at zero bromine concentration is $2{\cdot}33 \times 10^7$; if it is assumed that only one radical is involved and that f_1, f_2, and f_3 are unity, this corresponds to an initial recoil volume of radius 4·3 Å. However, this initial condition is not consistent with the (k_2t_0) term necessary to give the correct shape to the curve of retention against bromine concentration, unless a higher value of k_2 than that estimated in the present work is adopted.

The semi-empirical treatment of the diffusive processes given above accounts for most of the known features of Szilard–Chalmers reactions. Although the treatment of such reactions is naïve, and justified only by the convenience of its solution, a more realistic approach does not seem to be yet warranted in view of the uncertainty of several details of the process. In particular, reactions between radicals and other inactive species can only be inferred, and their real importance cannot be properly estimated; also, the relative importance of reactions involving the radio-bromine atom cannot be properly assessed, because knowledge of their activation energies is either lacking or too imprecise.

APPENDIX

The equations to be solved are (iv) and (v).

By integration of (iv) (omitting the last term) between the limits $t = 0$ and T,

$$\frac{1}{n_1(T)} = \exp\,(k_2cT)\left[\frac{1}{n_1(0)} + \frac{k_1}{\alpha}\int_0^T \frac{\exp\,(-k_2cs)}{(t_0 + s)^{3/2}}\,\mathrm{d}s\right] \quad . \quad . \quad . \quad . \quad \text{(xi)}$$

By integration of (v) between the limits $t = 0$ and ∞,

$$n_2(\infty) = n_2(0) \exp\left[-\frac{k_3}{\alpha}\int_0^\infty \frac{n_1(t)\,dt}{(t_0+t)^{3/2}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(xii)}$$

By rearrangement of (iv):

$$\frac{k_1 n_1(t)\,dt}{\alpha(t_0+t)^{3/2}} = -\left[k_2 c + \frac{1}{n_1(t)}\frac{dn_1(t)}{dt}\right]dt \quad . \quad . \quad . \quad . \quad . \qquad \text{(xiii)}$$

Integrating:

$$\frac{k_1}{\alpha}\int_0^\infty \frac{n_1(t)\,dt}{(t_0+t)^{3/2}} = \underset{T\to\infty}{\text{Lim.}} - \left[[k_2cT + \ln\frac{n_1(T)}{n_1(0)}\right] = \underset{T\to\infty}{\text{Lim.}} \ln\frac{n_1(0)}{n_1(T)}\exp(-k_2cT)$$

$$= \ln\left[1 + \frac{k_1 n_1(0)}{\alpha}\int_0^\infty \frac{\exp(-k_2cs)}{(t_0+s)^{3/2}}\,ds\right] \quad . \quad . \quad . \quad . \quad . \qquad \text{(xiv)}$$

by substitution from (xi).

From (xii) and (xiv),

$$\ln\left(\frac{(n_2(\infty)}{n_2(0)}\right) = -\frac{k_3}{k_1}\ln\left[1 + \frac{k_1 n_1(0)}{\alpha}\int_0^\infty \frac{\exp(-k_2cs)}{(t_0+s)^{3/2}}\,ds\right]$$

or

$$\frac{n_2(\infty)}{n_2(0)} = \left[1 + \frac{k_1 n_1(0)}{\alpha}\int_0^\infty \frac{\exp(-k_2cs)}{(t_0+s)^{3/2}}\,ds\right]^{-k_3/k_1} \quad . \quad . \quad . \quad . \qquad \text{(xv)}$$

The solution of the remaining integral is straightforward, and is:

$$\int_0^\infty \frac{\exp(-k_2cs)}{(t_0+s)^{3/2}}\,ds = \frac{2}{t_0^{\frac{1}{2}}}\left\{1 - \sqrt{\pi}(k_2ct_0)^{\frac{1}{2}}\exp(k_2ct_0)\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{\sqrt{(k_2ct_0)}}\exp(-z^2)dz\right]\right\}.$$

The authors are indebted to Professor M. H. L. Pryce, F.R.S., for his encouragement and for his solution of the differential equations.

THE CLARENDON LABORATORY, OXFORD.

[*Received, July* 19*th*, 1956.]