1007. *Kinetics of Free-radical Reactions in Solution. Part I. Evaluation of Rate Constants for Transfer Reactions in Systems with Varying Radical Concentrations.*

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The relation is derived between the rate constant for transfer and the final proportions of the various products in systems where free radicals, produced by a first-order decomposition, dimerize or undergo a radical-transfer reaction with the solvent.

RADICAL-TRANSFER reactions of the type, $A\cdot + B{-}C \longrightarrow A{-}B + C\cdot$, are difficult to study experimentally,[1] partly because of competing reactions and partly because of the difficulty of maintaining and measuring free-radical concentrations. A favoured radical source for quantitative study of these reactions has been the photolysis of ketones and other organic compounds,[2] but this method is not suitable for the production of all free radicals. An

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[1] Trotman-Dickenson, " Free Radicals: An Introduction," Methuen, London, 1959, p. 61.

[2] Steacie, " Atomic and Free Radicals Reactions," Reinhold, New York, 1954, Vol. I, p. 275.

alternative source, the pyrolysis of azo-compounds, peroxides, and organometallic compounds,[3] has the disadvantage of giving a radical concentration which decreases with time. This has led to the use of flow methods to maintain constant concentrations of radicals,[4] or consideration of initial rates only.[5] The approach described in this paper has various advantages. The experimental technique is simpler than that used for initial-rate studies, and the elaborate apparatus required for flow experiments is not needed. In addition, allowance can readily be made for " cage " recombination of radicals,[6] which makes the method particularly suitable for studying radical reactions in solution.

Consider the system:

$$\mathrm{MA_2} \longrightarrow \mathrm{M} + 2\mathrm{A}\cdot \qquad (1)$$

$$2\mathrm{A}\cdot \longrightarrow \mathrm{AA} \qquad (2)$$

$$\mathrm{A}\cdot + \mathrm{BH} \longrightarrow \mathrm{AH} + \mathrm{B}\cdot \qquad (3)$$

$$\mathrm{A}\cdot + \mathrm{B}\cdot \longrightarrow \mathrm{AB} \qquad (4)$$

$$2\mathrm{B}\cdot \longrightarrow \mathrm{BB} \qquad (5)$$

A thermal source of radicals MA_2 gives rise by a first-order reaction (1) to two radicals A•, which can either dimerize (2) or react with the solvent BH to produce a new radical B• (3). The radicals B• may either react with A• to give AB (4) or dimerize to give BB (5). The reaction mixture is heated in a thermostat-bath until all the MA_2 has decomposed ($\sim$20 half-lives). In the following treatment it is assumed (*a*) that no other reaction takes place, (*b*) that radical recombination is fast enough to ensure rapid attainment of steady state conditions, and (*c*) that the radicals A• and B• are similar in size and reactivity, so that the rate constants for reactions (2), (4), and (5) may be expected to be in the statistical proportions, $k_2 = k_5 = \frac{1}{2}k_4$.

Then at a given time:

$$\mathrm{d}[\mathrm{MA_2}]/\mathrm{d}t = -k_1[\mathrm{MA_2}]; \qquad (6)$$

$$\mathrm{d}[\mathrm{A}\cdot]/\mathrm{d}t = 2k_1[\mathrm{MA_2}] - 2k_2[\mathrm{A}\cdot]^2 - k_3[\mathrm{BH}][\mathrm{A}\cdot] - 2k_2[\mathrm{A}\cdot][\mathrm{B}\cdot] = 0; \qquad (7)$$

$$\mathrm{d}[\mathrm{B}\cdot]/\mathrm{d}t = k_3[\mathrm{A}\cdot][\mathrm{BH}] - 2k_2[\mathrm{A}\cdot][\mathrm{B}\cdot] - 2k_2[\mathrm{B}\cdot]^2 = 0. \qquad (8)$$

Let $$[\mathrm{B}\cdot] = [\mathrm{A}\cdot]\mathrm{X}, \qquad (9)$$

where X may be a function of time, concentrations, and rate constants. Eliminating [B•] from equation (8) we have

$$k_3[\mathrm{A}\cdot][\mathrm{BH}] - 2k_2\mathrm{X}[\mathrm{A}\cdot]^2 - 2k_2\mathrm{X}^2[\mathrm{A}\cdot]^2 = 0$$

or $$[\mathrm{A}\cdot] = k_3[\mathrm{BH}]/2k_2\mathrm{X}(1 + \mathrm{X}) \qquad (10)$$

Substitution of equation (9) and then of (10) in (7) gives

$$2k_1[\mathrm{MA_2}] - (k_3{}^2\mathrm{X}[\mathrm{BH}]^2 + k_3{}^2[\mathrm{BH}]^2)/2k_2\mathrm{X}^2(1 + \mathrm{X}) = 0,$$

or $$\mathrm{X} = \frac{[\mathrm{BH}]}{2[\mathrm{MA_2}]^{\frac{1}{2}}} \cdot \frac{k_3}{(k_1k_2)^{\frac{1}{2}}}. \qquad (11)$$

Since MA_2 is postulated to decompose by a first-order reaction, we have

$$[\mathrm{MA_2}] = [\mathrm{MA_2}]_0 \exp\,(-k_1t). \qquad (12)$$

If we set $$\frac{[\mathrm{BH}]}{2[\mathrm{MA_2}]_0{}^{\frac{1}{2}}} \cdot \frac{k_3}{(k_1\,.\,k_2)^{\frac{1}{2}}} = Z, \qquad (13)$$

then equation (11) becomes

$$\mathrm{X} = Z\exp(\tfrac{1}{2}k_1t), \qquad (14)$$

where Z is a constant for a given experiment.

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[3] Walling, " Free Radicals in Solution," Wiley, New York, 1957, p. 467.

[4] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, p. 102.

[5] Ref. 4, p. 197.

[6] Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.

Now the rates of production of AA, AB, and BB are given by equations (2), (4), and (5):

$$\mathrm{d[AA]/d}t = k_2[\mathrm{A}\cdot]^2; \tag{15}$$

$$\mathrm{d[AB]/d}t = 2k_2[\mathrm{A}\cdot][\mathrm{B}\cdot] = 2k_2\mathrm{X}[\mathrm{A}\cdot]^2; \tag{16}$$

$$\mathrm{d[BB]/d}t = k_2[\mathrm{B}\cdot]^2 = k_2\mathrm{X}^2[\mathrm{A}\cdot]^2. \tag{17}$$

Eliminating X and [A•] by use of equations (10), (11), (13), and (14) gives:

$$\frac{\mathrm{d[AA]}}{\mathrm{d}t} = \frac{k_1[\mathrm{MA_2}]_0 \exp{(-k_1t)}}{\{1 + Z\exp{(\frac{1}{2}k_1t)}\}^2}; \tag{18}$$

$$\frac{\mathrm{d[AB]}}{\mathrm{d}t} = \frac{2Zk_1[\mathrm{MA_2}]_0 \exp{(-\frac{1}{2}k_1t)}}{\{1 + Z\exp{(\frac{1}{2}k_1t)}\}^2}; \tag{19}$$

$$\frac{\mathrm{d[BB]}}{\mathrm{d}t} = \frac{Z^2k_1[\mathrm{MA_2}]_0}{\{1 + Z\exp{(\frac{1}{2}k_1t)}\}^2}. \tag{20}$$

The total quantity of each product is the integral of expressions (18), (19), or (20) between the limits $t = 0$ and $t = \infty$. Thus

$$[\mathrm{AA}] = \int_0^\infty \frac{k_1[\mathrm{MA_2}]_0 \exp{(-k_1t)}}{\{1 + Z\exp{(\frac{1}{2}k_1t)}\}^2}\cdot \mathrm{d}t. \tag{21}$$

Changing the variable to $t' = k_1t$ gives

$$[\mathrm{AA}] = [\mathrm{MA_2}]_0 \int_0^\infty \frac{\exp{(-t')}}{\{1 + Z\exp{(\frac{1}{2}t')}\}^2}\cdot \mathrm{d}t'. \tag{22}$$

Likewise we have

$$[\mathrm{AB}] = [\mathrm{MA_2}]_0 \int_0^\infty \frac{2Z\exp{(-\frac{1}{2}t')}}{\{1 + Z\exp{(\frac{1}{2}t')}\}^2}\cdot \mathrm{d}t'; \tag{23}$$

$$[\mathrm{BB}] = [\mathrm{MA_2}]_0 \int_0^\infty \frac{Z^2}{\{1 + Z\exp{(\frac{1}{2}t')}\}^2}\cdot \mathrm{d}t'. \tag{24}$$

If ratios of products are considered, the $[\mathrm{MA_2}]_0$ terms cancel. The values of the integrals depend only on Z, which in turn depends only on rate constants and initial concentrations, and is, therefore, a constant for a given experiment. The integrations, best carried out numerically, enable the correspondence of Z with [AA]/[AB] and [BB]/[AB] to be found. Since the product ratios can be measured experimentally, Z can be deduced, and thence by substitution in equation (13), the ratio of rate constants, $K = k_3/(k_1k_2)^{\frac{1}{2}}$, can be obtained.

The rate constant k_1 can normally be measured independently. If k_2, which has been measured or estimated for a number of reactions, is also known, the absolute value of k_3 can be determined. Even if k_2 is not known, the variation of $\log_{10} K$ with reciprocal temperature gives an estimate for the activation energy of the transfer reaction (3) since the activation energy of the dimerization (2) will be approximately zero. The Table illustrates the results.

Table of values of Z with corresponding [AA]/[AB] and [BB]/[AB] ratios.*

Z	[AA]/[AB]	[BB]/[AB]	Z	[AA]/[AB]	[BB]/[AB]	Z	[AA]/[AB]	[BB]/[AB]
0·3536	0·9247	0·3421	0·08839	3·327	0·1104	0·02628	10·38	0·04244
0·2973	1·085	0·2957	0·07433	3·908	0·09621	0·02210	12·24	0·03703
0·2500	1·274	0·2560	0·06250	4·593	0·08391	0·01858	14·44	0·03230
0·2102	1·495	0·2219	0·05256	5·400	0·07320	0·01562	17·05	0·02816
0·1768	1·754	0·1926	0·04419	6·352	0·06387	0·01314	20·15	0·02455
0·1487	2·058	0·1673	0·03716	7·477	0·05573	0·01105	23·81	0·02139
0·1250	2·414	0·1455	0·03125	8·806	0·04864			
0·1051	2·834	0·1267						

* To interpolate, take logarithms of all these quantities. $\mathrm{Log}_{10}\,Z$ is regularly spaced, and the logarithms of the ratios have quite small second differences, so that linear interpolation will be sufficiently accurate for most purposes.

More Complicated Systems.—If the two types of free radicals involved do not recombine in the statistical ratio assumed above, the kinetic expression is considerably more complicated. No analytical solution has been found (the equations involve the fourth power of the radical concentrations) but, if the relative values of the rate constants for the recombination reactions ($k_2 : k_4 : k_5$) are known, numerical methods allow solutions to be obtained for individual cases. An approximate value for $[\mathrm{B}\cdot]_n$ at a large value of t_n is obtained by assuming that $[\mathrm{A}\cdot]_n = 0$. This solution is refined by the Newton–Raphson method.[7] A new, smaller value of t is taken, and [A•] and [B•] are evaluated by the Newton–Raphson method, by using values obtained at t_n as a first approximation. This process is repeated to give values of [A•] and [B•] at various times during the experiment. From these values. the instantaneous rates of production of AA, AB, and BB at various times can be evaluated from the known relative recombination rates. The instantaneous production rates are then integrated numerically to give the product ratios for different values of Z, as in the simple case where $k_2 = \frac{1}{2}k_4 = k_5$. This calculation is best performed by an electronic computer.

The Cage Effect.—Most thermal sources of free radicals do not produce the theoretical number of free radicals in solution, as a proportion of the radicals dimerize before they can diffuse apart out of the solvent " cage " surrounding the $\mathrm{MA_2}$ molecule.[6] This results, in the system considered in this paper, in a value of [AA]/[AB] greater than that expected from the corresponding value of [BB]/[AB]. The difference $[\mathrm{AA}]_{\text{found}} - [\mathrm{AA}]_{\text{expected}}$, when expressed as a percentage of [AA] + [AB] + [BB], gives the proportion of radical source which does not give rise to free radicals. The corrected value $[\mathrm{MA_2}]_0\ (1 - \frac{\text{“ cage \% ”}}{100})$ should in these circumstances be the value introduced into equation (13) when experimental results are interpreted, as the remainder of the $\mathrm{MA_2}$ plays no part in the reaction sequence considered.

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[7] See Margenau and Murphy, " The Mathematics of Physics and Chemistry," Van Nostrand, Princeton, 1956, p. 492.