have a greater tendency to bring potential reactants together than will uncorrelated displacements.

The same qualitative conclusion is suggested by noting that for a very efficient stationary sink the radial distribution function is nearly the same whether the diffusion coefficient of species toward it is D or $2D$, although of course the flux is different for the two cases. Any diffusive motion of the reference molecule in a sink will permit it to sample regions of higher concentration of potential reactants and should increase reactivity.

Both of the above qualitative arguments suggest that the derivation of eq. 1 and 3 contains an approximation that deserves more quantitative treatment. However, such a treatment would apparently predict a larger rate constant than that calculated with the use of these equations. Since the discrepancy indicated in Table I is in the opposite direction, the moving sink effect merely reinforces the failure of the data to satisfy the predictions of theory.

Isotropic Medium Approximation.—The derivation of the equations assumes that the relative diffusion coefficient of two iodine atoms is independent of their separation. The experiments measured the bulk diffusion coefficient of isolated atoms in the solvent. When two atoms become separated by distances of the order of a molecular diameter or less, distributions of adjacent solvent molecules certainly exert nonrandom forces that influence the directions of relative displacements by the atoms. Although these nonrandom effects involve very small volumes of solution and are operative for an infinitesimal fraction of the lifetime of an atom, they can greatly influence observed rate constants.

These directional effects of solvent molecules apparently offer the best explanation for the discrepancies in Table I. As two iodine atoms diffuse toward each other, they are less apt to undergo a collision than they would be if the medium were a true continuum through which they moved with the same behavior as that of their bulk diffusion.

Although this effect causes the rate constant for recombination to be less than that predicted by a continuum model, the equilibrium constant for iodine dissociation is almost the same in solution and in gas phase.[12] Hence the same effect must also operate to reduce the rate of thermal dissociation. This prediction is supported by the effect of wave length on the quantum yield for dissociation of iodine in solution.[10] As the energy of the absorbed quantum increases, the quantum yield increases more rapidly than would be expected if the surrounding medium were a viscous continuum. The behavior has been explained[13] by an argument similar to that employed here.

In carbon tetrachloride at 25°, the measured value of D is 2.7 times the value predicted by eq. 3.[7] In hexane, the same ratio is 1.5.[8] The difference is in the direction to be expected from the effect of solvent on quantum yield,[13,14] but the data in hexane are not extensive enough to justify rigorous quantitative comparisons.

Since the "cage" effect was first proposed by Rabinowitch,[9] it has not been clear whether it was necessary to invoke specific energy barriers in order to account for observations. Thus, models that assumed completely random displacements in an isotropic continuum[15] appeared to offer a satisfactory description of most experiments. The measurements of quantum yield[13] and of diffusion coefficient[7] now make it necessary to postulate a small but significant potential barrier to the separation or bringing together of two reactive species. These experiments use pairs of very reactive atoms to probe small regions of space for very short times and to learn the degree of confidence to place in the mathematically tractable models that treat the medium as a continuum. Apparently it is unwise to assume that the absolute predictions of such models are valid to better than a factor of two, although the models may predict ratios of quantities more accurately than this.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(45-1)-1310.

[12] M. Gazith and R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 6091 (1955).

[13] R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).

[14] D. Booth and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1868 (1960).

[15] R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); **23**, 1982 (1955); *J. Am. Chem. Soc.*, **77**, 2042 (1955); **78**, 5486 (1956); *J. Phys. Chem.*, **65**, 763 (1961).

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A Kinetic Analysis of Short-Chain, Radiation-Initiated Addition Reactions

BY L. H. GALE AND C. D. WAGNER

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Kinetic expressions for product yields in short-chain, radiation-initiated free-radical addition reactions have been developed in a novel way, based upon radiation yields. It is shown by using model systems involving addition of isopropyl alcohol and isopropylamine to α-olefins that effects of reaction variables on yield of 1:1 adduct and ratios of 1:1 to 1:2 adduct are as predicted. A procedure is developed for using short-chain reactions to determine transfer constants. The true kinetic chain length of a chain reaction includes a contribution from the reaction $A\cdot + AB \rightarrow AB + A\cdot$, which, of course, is ordinarily unobserved. An isotopic experiment shows that in the systems under study it is unimportant. It is concluded that the conventional chain length for such reactions is close to the true chain length.

Ionizing radiation is generally useful for initiating free-radical addition reactions. Radiation initiation offers several advantages for kinetic studies. These include: (1) independence of initiation rate on temperature, and (2) uniform (or variable) rate of formation of initiator radicals. A number of kinetic-type investigations using radiation initiation have been reported, including the addition of carbon tetrachloride to β-pinene[1]

[1] R. L. Webb, *Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, 2nd; Geneva*, **29**, 331 (1958).

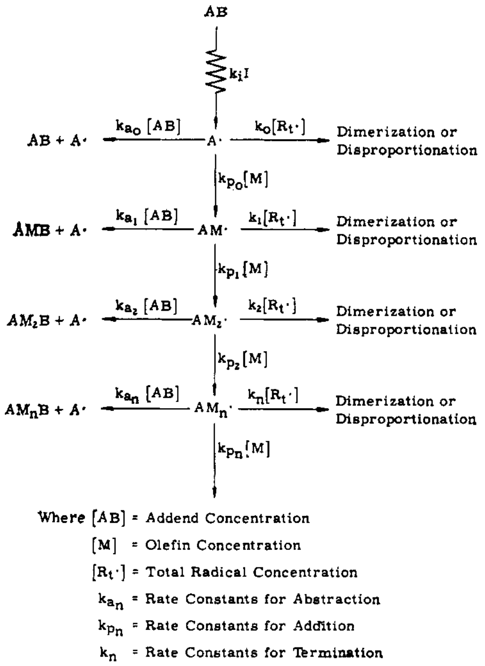

Fig. 1.—Over-all reaction scheme.

and ethylene,[2] *n*-butyl mercaptan to 1-pentene[3] and 1-octene,[4] hydrogen bromide to ethylene,[5] isopropyl alcohol to ethylene,[6] chloroform to ethylene,[7] bromotrichloromethane to butadiene,[8] isoprene, and 2,3-dimethylbutadiene,[9] and acetaldehyde to ethylene,[10] propylene,[11] and isobutylene.[12] All of these investigations have in common the study of addition reactions of long kinetic chain length with the attendant simplification of kinetic expressions. Furthermore, several of the reactions yield primarily the simple 1:1 adduct and are not complicated by the formation of higher addition products (telomers).

With the uniform initiation rate that is possible using ionizing radiation, it becomes feasible to develop useful kinetic expressions for short-chain reactions as well as for those having long kinetic chains. These have been derived in the present investigation and tested qualitatively with model reactions: the addition of isopropylamine to 1-pentene and isopropyl alcohol to 1-butene and 1-pentene. (Urry and co-workers[13,14] had demonstrated the short-chain character of these reactions using peroxide and light initiation.)

Derivation of Kinetic Expressions.—The over-all course of a radiation-initiated, free-radical addition reaction may be represented by the sequence in Fig. 1. Termination is assumed to occur by bimolecular radical combination or disproportionation, and initiation rate is assumed to be uniform. The following novel treatment is based upon 100-e.v. yield (*G*-value) rather than upon reaction rate.

An initial 100-e.v. yield of radicals, A·, is assumed and is represented by G_{A_1}. The fraction of these radicals which abstract B from AB to yield the starting material and A· is

$$\frac{k_{a_0}[\mathrm{AB}]}{k_{a_0}[\mathrm{AB}] + k_{p_0}[\mathrm{M}] + k_0[\mathrm{R_t}\cdot]}$$

Let $k_{a_0}[\mathrm{AB}] = a_0$, let $k_{p_0}[\mathrm{M}] = p_0$, and let $k_{a_0}[\mathrm{AB}] + k_{p_0}[\mathrm{M}] + k_0[\mathrm{R_t}\cdot] = z_0$. Then from the reaction of first-formed A·, the yield of AB is $G_{\mathrm{AB}} = (a_0/z_0)(G_{A_1})$. Similarly, the fraction of the first-formed radicals, A·, which add to olefin, M, to yield the new radical, AM·, is p_0/z_0, and $G_{\mathrm{AM}\cdot} = (p_0/z_0)(G_{A_1})$.

The fraction of radicals, AM·, which abstract B from AB to yield the 1:1 adduct, AMB, is

$$\frac{k_{a_1}[\mathrm{AB}]}{k_{a_1}[\mathrm{AB}] + k_{p_1}[\mathrm{M}] + k_1[\mathrm{R_t}\cdot]}$$

Let $k_{a_1}[\mathrm{AB}] = a_1$, let $k_{p_1}[\mathrm{M}] = p_1$, and let $k_{a_1}[\mathrm{AB}] + k_{p_1}[\mathrm{M}] + k_1[\mathrm{R_t}\cdot] = z_1$. Then $G_{\mathrm{AMB}} = (a_1/z_1)(G_{\mathrm{AM}\cdot})$. But $G_{\mathrm{AM}\cdot} = (p_0/z_0)(G_{A_1})$. Thus $G_{\mathrm{AMB}} = (a_1p_0/z_1z_0)\cdot(G_{A_1})$.

By use of the same type of reasoning and notation, $G_{\mathrm{AM_2}\cdot} = (p_1p_0/z_1z_0)(G_{A_1})$ and $G_{\mathrm{AM_2B}} = (a_2p_1p_0/z_2z_1z_0)(G_{A_1})$.

It is then easily derived that

$$G_{\mathrm{AM}_n\mathrm{B}} = \frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}(G_{A_1})$$

where $a_n = k_{a_n}[\mathrm{AB}]$; $z_n = k_{a_n}[\mathrm{AB}] + k_{p_n}[\mathrm{M}] + k_n[\mathrm{R_t}\cdot]$; $p_i = k_{p_i}[\mathrm{M}]$; $z_i = k_{a_i}[\mathrm{AB}] + k_{p_i}[\mathrm{M}] + k_i[\mathrm{R_t}\cdot]$.

For each molecule of product, $\mathrm{AM}_n\mathrm{B}$, a free radical A· is regenerated. The yield of regenerated A·, G_{A_2}, is given by

$$G_{A_2} = G_{\mathrm{AB}} + G_{\mathrm{AMB}} + G_{\mathrm{AM_2B}} + \ldots + G_{\mathrm{AM}_n\mathrm{B}} = \sum_{n=0}^{\infty} G_{\mathrm{AM}_n\mathrm{B}} = \sum_{n=0}^{\infty}\frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}G_{A_1}$$

On this second cycle, starting with regenerated A·, the added yields of product species are given by similar expressions, this time in terms of G_{A_2}: $G_{\mathrm{AB}} = (a_0/z_0)G_{A_2}$, $G_{\mathrm{AMB}} = (a_1p_0/z_1z_0)G_{A_2}$, and

$$G_{\mathrm{AM}_n\mathrm{B}} = \frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}G_{A_2}$$

On the third cycle, the similar sequence will occur where

$$G_{A_3} = \sum_{n=0}^{\infty}\frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}G_{A_2}$$

But

$$G_{A_2} = \sum_{n=0}^{\infty}\frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}G_{A_1}$$

Then

$$G_{A_3} = \left[\sum_{n=0}^{\infty}\frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}\right]^2 G_{A_1}$$

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(2) C. David and P. A. Gosselain, *Tetrahedron*, **18**, 639 (1962).

(3) A. Fontijn and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1384, 1397, 1410 (1957).

(4) W. H. Clingman, Jr., *J. Phys. Chem.*, **64**, 1355 (1960).

(5) D. A. Armstrong and J. W. T. Spinks, *Can. J. Chem.*, **37**, 1210 (1959).

(6) K. Hirota and M. Hatada, *Bull. Chem. Soc. Japan*, **34**, 1644 (1961).

(7) F. W. Mellows and M. Burton, *J. Phys. Chem.*, **66**, 2164 (1962).

(8) C. S. Hsia Chen and R. F. Stamm, *J. Org. Chem.*, **28**, 1580 (1963).

(9) C. S. Hsia Chen and E. F. Hosterman, *ibid.*, **28**, 1585 (1963).

(10) K. Hirota, S. Iizuka, H. Ochi, and M. Hatada, *Bull. Chem. Soc. Japan*, **36**, 115 (1963).

(11) K. Hirota and M. Hatada, *ibid.*, **33**, 1682 (1960).

(12) S. Iizuka, M. Hatada, and K. Hirota, *ibid.*, **36**, 817 (1963).

(13) W. H. Urry, O. O. Juveland, and F. W. Stacey, *J. Am. Chem. Soc.*, **74**, 6155 (1952).

(14) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *ibid.*, **76**, 450 (1954).

On the fourth cycle, the yield of regenerated A · is given by

$$G_{A_4} = \sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} G_{A_3}$$

Then

$$G_{A_4} = \left[\sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i}\right]^3 G_{A_1}$$

The total yield of radicals A· is then the sum of the A· formed by regeneration during each cycle added to that formed by the primary irradiation.

$$\sum_{n=1}^{\infty} G_{A_n} = G_{A_1} + G_{A_2} + G_{A_3} + G_{A_4} + \ldots + G_{A_n}$$

Substituting for each G_A gives a convergent series whose sum is given by

$$\sum_{n=1}^{\infty} G_{A_n} = G_{A_1}\left(\frac{1}{1 - \left[\sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i}\right]}\right)$$

where the expression

$$\left[\sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i}\right]$$

is the fraction of radicals regenerated in each cycle and is denoted below by f. The development at this stage is rigorous for the reaction model assumed, and applies to both long- and short-chain reactions.

Kinetic Chain Length.—The total yield (G-value) of all adducts formed is equal to the total yield of regenerated radicals A·. Thus the yield of $\sum_{n=0}^{\infty} G_{AM_nB}$, and of radicals formed by abstraction, is given by

$$\sum_{n=0}^{\infty} G_{AM_nB} = \sum_{n=1}^{\infty} G_{A_n} - G_{A_1} = G_{A_1}\left(\frac{1}{1-f}\right) - G_{A_1} = G_{A_1}\left(\frac{f}{1-f}\right)$$

The important quantity in determining the chain length of the radical addition reaction is the average number of abstraction reactions per initiating radical, a quantity which we define here as the *true* kinetic chain length. It is derived from the above expression and is given by

$$\frac{\sum_{n=0}^{\infty} G_{AM_nB}}{G_{A_1}} = \frac{f}{1-f} = \frac{\sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i}}{\left(1 - \sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i}\right)}$$

where $a_n = k_{a_n}[AB]$, $p_i = k_{p_i}[M]$, and $z_n = k_{a_n}[AB] + k_{p_n}[M] + k_n[R_t\cdot]$. The complexity of this rigorous expression requires several simplifying assumptions in order to assess the qualitative effect of reaction variables on the true kinetic chain length. For this purpose, we may assume equal rate constants for all abstraction reactions, $k_{\bar{a}}$, equal constants for all addition reactions, $k_{\bar{p}}$, and equal constants for all termination reactions, $k_{\bar{t}}$. Then

$$\sum_{n=0}^{\infty} \frac{a_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \cong \frac{k_{\bar{a}}[AB]}{k_{\bar{a}}[AB] + k_{\bar{t}}[R_t\cdot]}$$

The true kinetic chain length, L, becomes

$$L = \frac{\sum_{0}^{n} G_{AM_nB}}{G_{A_1}} \cong \frac{k_{\bar{a}}[AB]}{k_{\bar{t}}[R_t\cdot]}$$

It is then the ratio of the rate of abstraction to the rate of termination (or initiation) and is analogous to the kinetic chain length in a polymerization reaction, *i.e.*, the ratio of the rate of propagation to the rate of termination (or initiation). It should be noted that the true kinetic chain length is not the same as the observed chain length ordinarily considered in such reactions. This is the ratio of moles of observable product to moles of initiating radicals and is given rigorously by

$$L = \frac{\sum_{1}^{n} G_{AM_nB}}{G_{A_1}} = \frac{f - \frac{k_{a_0}[AB]}{k_{a_0}[AB] + k_{p_0}[M] + k_0[R_t\cdot]}}{1-f}$$

If $k_{a_0}[AB]$ is small relative to $k_{p_0}[M]$, the observed chain length approaches the true kinetic chain length. It is apparent that the propagation reaction (addition to unsaturate to make larger radicals) has no direct influence on the kinetic chain length, but it is essential for forming observable product.

The kinetic chain length is a direct function of addend concentration and of temperature, since the abstraction reaction ordinarily has an activation energy of 5–8 kcal./mole while the termination reactions are not temperature sensitive. The chain length in this reaction scheme is an inverse function of dose rate, since free-radical concentration is proportional to the dose rate to the one-half power.

Experimentally, the true chain length can be determined if one can measure the total yields (G-values) of all the adducts, AM_nB (including AM_0B), and divide by the yield of radicals formed by radiation. However, ordinarily only the adducts AMB, AM_2B, and sometimes AM_3B can be measured. Higher adducts may be roughly estimated from the relative yields of lower ones, but an ordinarily impossible task is the determination of the yield of the product AM_0B which is chemically the same as the addend. This reaction, if it is fast, could be a major contributor to the kinetic chain length.

An experiment was performed to determine whether this ordinarily unseen reaction is important. A mixture of isopropyl alcohol, isopropyl-d_7 alcohol, and 1-butene was irradiated. The yields of observable products were determined, and the yield of AM_0B was determined from the yields of isopropyl-d_1 alcohol and isopropyl-d_6 alcohol.

$$\left.\begin{matrix}\cdot C_3D_6OH \\ \\ \cdot C_3H_6OH\end{matrix}\right\} + \left\{\begin{matrix}C_3D_7OH \\ \\ C_3H_7OH\end{matrix}\right. \longrightarrow \begin{matrix}C_3D_7OH \\ C_3HD_6OH \\ C_3H_6DOH \\ C_3H_7OH\end{matrix} + \left\{\begin{matrix}\cdot C_3D_6OH \\ \\ \cdot C_3H_6OH\end{matrix}\right.$$

Results (see below) demonstrated that under the conditions used the G-value for compound AM_0B is less than 1.6, while that for AM_1B is 5.6, AM_2B is 0.90, and AM_3B is 0.27. Thus, the conventional chain length is at least 80% of the true chain length. This reaction to form AM_0B is probably usually of minor importance, because it is thermochemically neutral, whereas the propagation reaction is exothermic.

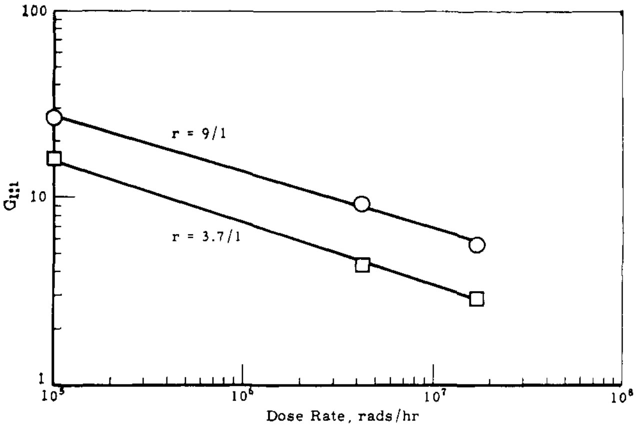

Fig. 2.—Effect of dose rate on $G_{1:1}$ for addition of isopropylamine to 1-pentene at 100°.

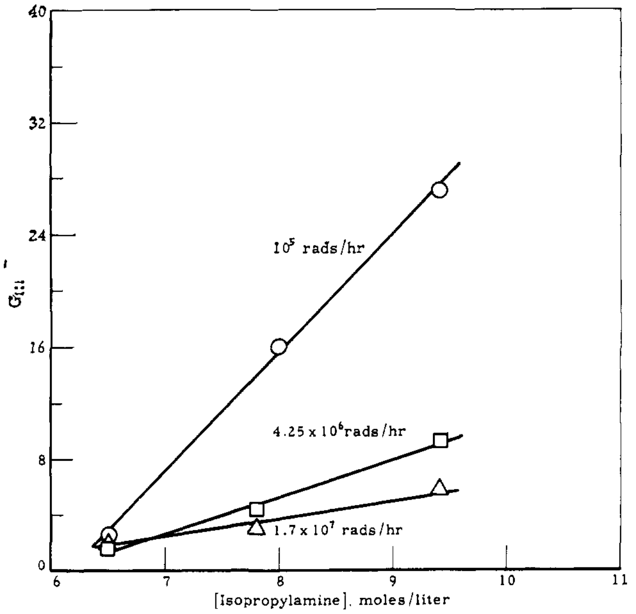

Fig. 3.—Effect of addend concentration on $G_{1:1}$ for addition of isopropylamine to 1-pentene at 100°.

Yield of 1:1 Adduct.—The yield of adduct AM_nB is given by the general expression

$$G_{AM_nB} = \frac{a_n}{z_n}\prod_{i=0}^{n-1}\frac{p_i}{z_i}\left(\frac{1}{1-\sum\limits_{n=0}^{\infty}\frac{a_n}{z_n}\prod\limits_{i=0}^{n-1}\frac{p_i}{z_i}}\right)G_{A\cdot}$$

In the case of the 1:1 adduct, AMB, the yield is given by

$$G_{AMB} = \frac{a_1p_0}{z_1z_0}\left(\frac{1}{1-\sum\limits_{n=0}^{\infty}\frac{a_n}{z_n}\prod\limits_{i=0}^{n-1}\frac{p_i}{z_i}}\right)G_{A\cdot}$$

Clearly this expression is a complex function of a number of rate constants. To obtain the qualitative effect of reaction variables, we again simplify by making the assumption of equal rate constants for all abstraction reactions, $k_{\bar{a}}$, all addition reactions, $k_{\bar{p}}$, and all termination reactions, $k_{\bar{t}}$. An additional simplification can be made by omitting the initial abstraction reaction of A· radical; *i.e.*, $k_{a_0} \simeq$ zero from isotopic study. The expression for the yield of AMB then simplifies to

$$G_{AMB} \cong \frac{k_{\bar{a}}[AB]k_{\bar{p}}[M](k_{\bar{a}}[AB] + k_{\bar{t}}[R_t\cdot])G_{A\cdot}}{(k_{\bar{a}}[AB] + k_{\bar{p}}[M] + k_{\bar{t}}[R_t\cdot])(k_p[M] + k_{\bar{t}}[R_t\cdot])k_{\bar{t}}[R_t\cdot]}$$

At sufficiently low dose rate, where $k_{\bar{t}}[R_t\cdot]$ becomes small relative to $k_{\bar{a}}[AB]$ and $k_{\bar{p}}[M]$, then

$$G_{AMB} \cong \frac{(k_{\bar{a}}[AB])^2}{(k_{\bar{a}}[AB] + k_{\bar{p}}[M])k_{\bar{t}}[R_t\cdot]}G_{A\cdot} \qquad (1)$$

and G_{AMB} will be a direct function of temperature and concentration of addend and an inverse function of dose rate (*ca.* $I^{0.5}$). At sufficiently high intensity, where relatively few initiating radicals form product by abstraction

$$G_{AMB} \cong \frac{k_{\bar{a}}[AB]k_{\bar{p}}[M]}{(k_{\bar{t}}[R_t\cdot])^2}G_{A\cdot} \qquad (2)$$

G_{AMB} will be a direct function of temperature, nearly independent of addend concentration in a binary mixture and a stronger inverse function of dose rate.

The effects of these reaction variables on the yield of 1:1 adduct formed in the addition of isopropylamine to 1-pentene are summarized in Fig. 2, 3, and 4. The dose rate dependence over the range studied is $I^{-0.33}$. Apparently the dose rate was not sufficiently high to observe the stronger inverse dependence predicted by expression 2. The effects of dose rate, addend concentration, and temperature are in qualitative agreement with the predicted effects.

Ratio of Adducts and Evaluation of Transfer Constants.—A relationship which yields useful kinetic data is the expression for the ratio of two consecutive adducts. The ratio of the yields of two consecutive adducts is given by the following expression

$$\frac{G_{AM_nB}}{G_{AM_{n-1}B}} = \frac{\frac{a_n}{z_n}\prod\limits_{i=0}^{n-1}\frac{p_i}{z_i}\sum G_{A\cdot}}{\frac{a_{n+1}}{z_{n+1}}\prod\limits_{i=0}^{n}\frac{p_i}{z_i}\sum G_{A\cdot}} = \frac{a_nz_{n+1}}{a_{n+1}p_n}$$

Substituting the appropriate rate constants and con-

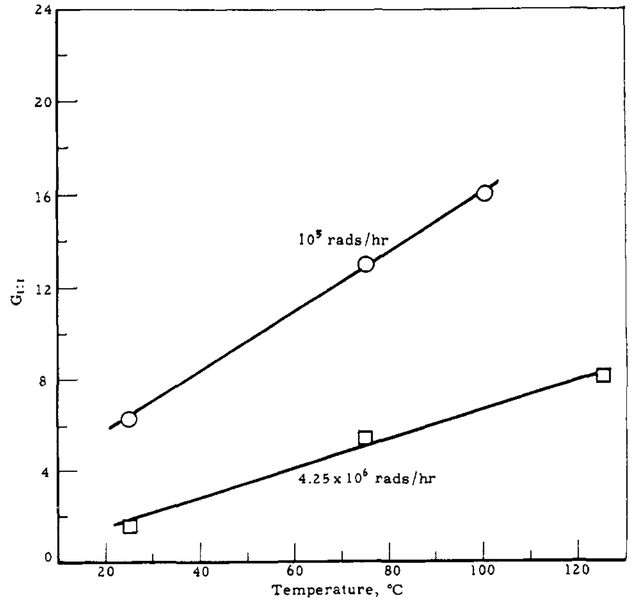

Fig. 4.—Effect of temperature on $G_{1:1}$ for addition of isopropylamine to 1-pentene (r = 4.0/1).

centrations for the various symbols gives, without approximations

$$\frac{G_{AM_nB}}{G_{AM_{n+1}B}} = \frac{k_{a_n}k_{n+1}[R_t\cdot]}{k_{a_{n-1}}k_{p_n}[M]} + \frac{k_{a_n}[AB]}{k_{p_n}[M]} + \frac{k_{a_n}k_{p_{n+1}}}{k_{a_{n-1}}k_{p_n}}$$

Let $C_n = k_{a_n}/k_{p_n}$, $C_{n+1} = k_{a_{n+1}}/k_{p_{n+1}}$, and $r = [AB]/[M]$. Then

$$\frac{G_{AM_nB}}{G_{AM_{n-1}B}} = \frac{C_n}{k_{a_{n-1}}[M]} k_{n+1}[R_t\cdot] + C_n r + \frac{C_n}{C_{n+1}}$$

If the chain is long, $k_{n+1}[R_t\cdot]$ is small and the ratio of the yields of the two products is simply given by

$$\frac{G_{AM_nB}}{G_{AM_{n-1}B}} = C_n r + \frac{C_n}{C_{n+1}}$$

Mellows and Burton[7] derived an identical expression from conventional rate equations for calculating transfer constants in the long-chain, radiation-initiated addition of chloroform to ethylene. However, where $k_{n+1}[R_t\cdot]$ cannot be ignored, in reactions with short chains the solution is more complex, but is still capable of solution by the treatment below.

With bimolecular termination and the assumption of a single effective rate constant for termination, k, the total steady-state free-radical concentration, $[R_t\cdot]$, will equal $(k_iI/k_t)^{0.5}$. Substitution of this for $[R_t\cdot]$ leads to the following relationship between the ratio of two consecutive adducts and dose rate, I

$$\frac{G_{AM_nB}}{G_{AM_{n+1}B}} = \frac{C_n(k_ik_t)^{0.5}}{k_{a_{n+1}}[M]} I^{0.5} + \left[C_n r + \frac{C_n}{C_{n+1}}\right] \quad (3)$$

A plot of $G_{AM_nB}/G_{AM_{n-1}B}$ *vs.* (dose rate)$^{0.5}$ should be a straight line. As dose rate is decreased, the chain length increases, and the y-intercept at zero dose rate provides the quantity characteristic of long chains

$$y\text{-intercept} = \left(\frac{G_{AM_nB}}{G_{AM_{n+1}B}}\right)_{I=0} = C_n r + \frac{C_n}{C_{n+1}} \quad (4)$$

The absolute values of C_n and C_{n+1} (transfer constants) can be determined by a second graphical procedure by plotting y-intercepts for two or more r-values *vs.* r. The slope of the resulting straight line is equal to C_n and the new y-intercept is equal to C_n/C_{n+1}.

If the chain length of the addition reaction is long, the measured yields of two consecutive adducts approach $(G_{AM_nB}/G_{AM_{n+1}B})_{I=0}$ and the operation involving eq. 3 is unnecessary; instead, eq. 4 is directly applicable.

In order to evaluate the validity of the expression relating the ratio of $G_{AM_nB}/G_{AM_{n-1}B}$ to dose rate, three synthetic mixtures of isopropylamine–1-pentene and isopropyl alcohol–1-pentene were prepared and irradiated at three dose rates at 100°. The total dose was varied in order to maintain the conversion of olefin to product below 10 mole %. Usually the conversion was 1–5%. Low conversion minimized the change in the [addend]/[olefin] ratio during the course of the reaction. The products were analyzed in each case by gas–liquid phase chromatography. The ratios of the G_{AMB}/G_{AM_2B} were calculated directly from the areas under the appropriate peaks.

Plots of G_{AMB}/G_{AM_2B} *vs.* (dose rate)$^{0.5}$ are shown in Fig. 5 and 6. Within experimental error, the ratio G_{AMB}/G_{AM_2B} does increase linearly with (dose rate)$^{0.5}$ as predicted by eq. 3.

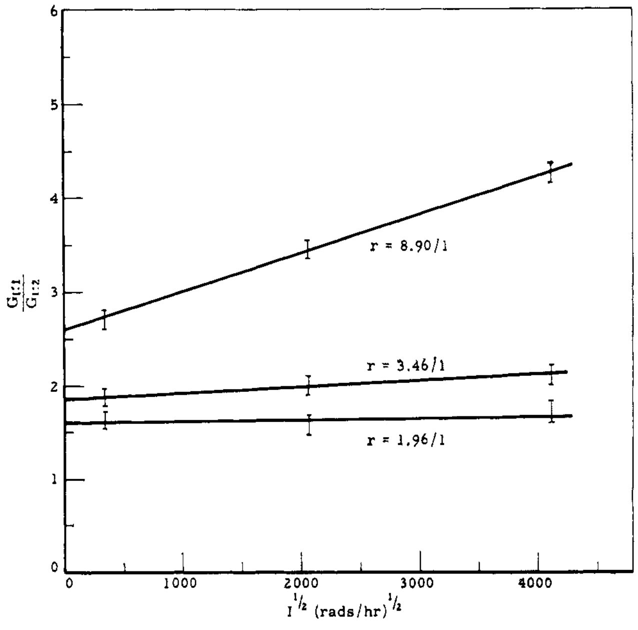

Fig. 5.—Effect of dose rate on $G_{1:1}/G_{1:2}$ for isopropylamine and 1-pentene at 100°.

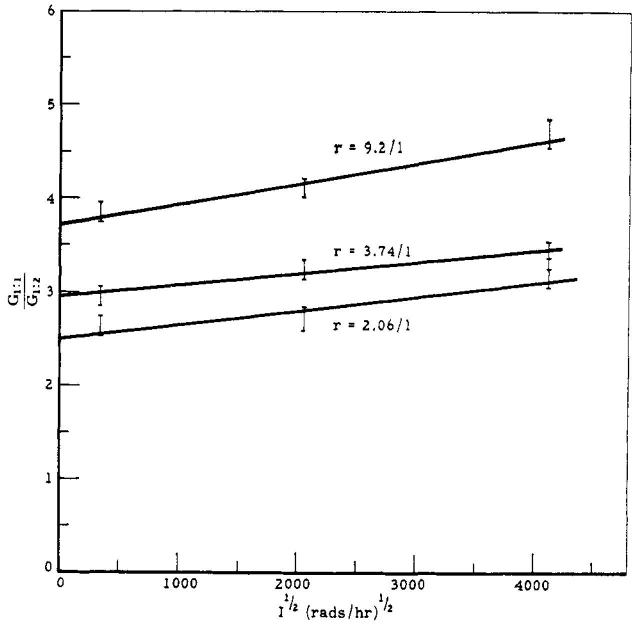

Fig. 6.—Effect of dose rate on $G_{1:1}/G_{1:2}$ for isopropyl alcohol and 1-pentene at 100°.

In Fig. 7, the y-intercepts obtained from Fig. 5 and 6 are plotted *vs.* the appropriate r-values. Good straight lines are obtained for both the addition of isopropylamine and isopropyl alcohol. The values for C_1 calculated from the slopes were 0.145 ± 0.018 and 0.169 ± 0.036, respectively. Values for C_2 calculated from the intercepts were 0.110 ± 0.021 and 0.081 ± 0.024, respectively.

The absolute magnitude of these transfer constants are in reasonably good agreement with those reported in the literature, particularly the values of C_2 compared to Urry's C_{av} of 0.095 for isopropylamine and 0.052 for isopropyl alcohol obtained in the peroxide-initiated addition to 1-octene at 120°.[13,14]

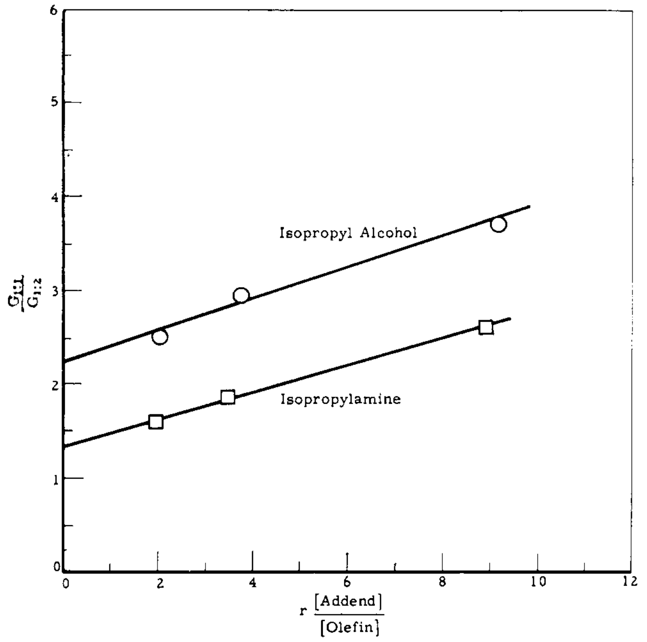

Fig. 7.—Effect of reactant concentration ratio on yield of adducts at zero dose rate.

Experimental

Reagents.—1-Butene (Phillips Research Grade) was used directly with no purification. 1-Pentene (Phillips Pure Grade), isopropyl alcohol (Eastman Organic Spectro Grade), and isopropylamine (Eastman Organic Chemicals) were dried over suitable reagents and fractionated through a 60-cm. Piros-Glover spinning-band column in a nitrogen atmosphere. The purified material was stored under nitrogen until used. The minimum purity in each case was greater than 99.5%.

Isopropyl-d_7 alcohol was synthesized as follows: acetone-d_6 (Volk Radiochemical Co.) was hydrogenated with deuterium at 100° and 200 p.s.i. with platinum oxide as catalyst. Hydroxylic deuterium was replaced by protium by successive treatments with 30-fold excesses of ethylene glycol, with isolation of product by distillation. Gas chromatographic analysis showed it to be 99.8+% chemically pure. Isotopic analysis by mass spectral examination of the bromide (see below) showed it to consist of 93% isopropyl-d_7 alcohol and 7% isopropyl-d_6 alcohol.

Irradiations.—Irradiations were carried out on 1-ml. degassed samples sealed *in vacuo* in 13 × 100 mm. heavy-walled Pyrex ampoules. High dose rates (>10^6 rads/hr.) were obtained with bremsstrahlung generated by 3-Mev. Van de Graaff electrons impinging on a gold target. The dose rates were determined by ceric dosimetry. Lower dose rate irradiations were carried out in a 10,000-curie cobalt-60 facility. The dose rates were determined by ferrous dosimetry.

Analysis.—The quantitative analysis of the liquid products was accomplished by programmed gas chromatographic analysis. The products from the addition of isopropyl alcohol to 1-butene and 1-pentene were resolved on a Ucon column (6 mm. o.d. × 1.5 m. long). The products from the addition of isopropylamine to 1-pentene were resolved on a KOH–Quadrol column (6 mm. o.d. × 1.5 m. long). With the exception of acetone, where the response was determined, relative peak areas were assumed to represent relative per cent by weight. Analysis for vicinal glycol was made by a periodate–thiosulfate volumetric method.

The analysis for $(CH_3)_2CDOH$ and $(CH_3)_2CHOH$ in the product from the addition of the isopropyl alcohol–isopropyl alcohol-d_7 mixture to 1-butene was made as follows: a 50-μl. sample of the product was separated by gas chromatography on a Ucon column and the isopropyl alcohol components trapped at −196°. The isolated alcohol fraction was converted to the bromide by treatment with excess phosphorus tribromide for 2 hr. at 23°. The purified isopropyl bromide was then analyzed for isotopic composition by mass spectral techniques. Isopropyl bromide is especially useful for this analysis since the parent ion sensitivity is high and there are no contributions by C_3 ions having fewer hydrogen atoms. A separate test confirmed that hydrogen exchange is not induced by the halogenation reaction.

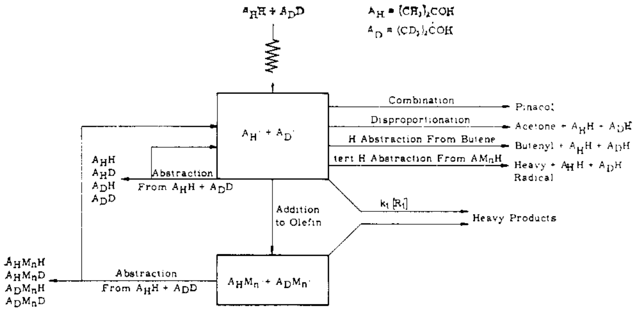

Fig. 8.—Formation and reactions of the isotopic hydroxypropyl radicals.

Identification of products was accomplished by trapping the gas chromatographically separated components and analyzing each component by mass and infrared spectrometry. The products identified in this manner are the 1:1 and 1:2 adducts in all three systems plus the 1:3 adduct from isopropyl alcohol and 1-butene.

Determination of Yield of AM_0B.—Two experiments were performed at 100° utilizing a mixture of isopropyl-d_7 alcohol, isopropyl alcohol, and 1-butene at a mole ratio of 5:5:1. Data obtained are shown in Table I.

Table I

Addition of Isopropyl Alcohol–Isopropyl Alcohol-d_7 to 1-Butene

Dose, Mrads	20.5		72.7	
Dose rate, Mrad/hr.	0.102		0.90	
Product composition	Wt. %[a]	G	Wt. %[a]	G
1-Butene	4.6		0.25	
Acetone	0.05	0.38	0.39	0.89
Isopropyl alcohol	91		91	
1:1 adduct	1.6	6.3	4.8	5.6
1:2 adduct	0.71	1.9	1.2	0.90
1:3 adduct	0.27	0.55	0.45	0.27
Pinacol	0.47	1.8	0.67	0.75
Unidentified	0.36		0.99	
	Mole %[b]	G	Mole %[b]	G
$(CD_3)_2CHOH$	<0.1	<0.6	0.97	1.9
$(CH_3)_2CDOH$	<0.1	<0.6	0.1	0.2

[a] The absolute accuracy of the analysis is estimated at ±10% of the listed values. [b] Mole per cent in recovered isopropyl alcohol–isopropyl alcohol-d_7 corrected for initial isotopic composition.

Reactions involving the hydroxypropyl radicals are shown in Fig. 8. The steady-state isotopic composition of $A_H\cdot$ and $A_D\cdot$ is determined by isotope effects in the formation by radiolysis and by hydrogen abstraction, and in the various reactions of the radicals. The latter involve only secondary isotope effects of low magnitude. The isotope effect in formation by radiolysis is small (1.3, judging from the study by Burr[15] on isotopic ethanol radiolysis). However, abstraction reactions by radicals should be subject to a large isotope effect. Urry[16] found that a methyl radical abstracts a hydrogen atom from the central carbon atom of isopropyl alcohol 6.3 times faster than a deuterium atom from the same position. Therefore, it might be expected that the steady-state concentration of $A_H\cdot$ should be about six times that of $A_D\cdot$. This appears to be true. The mass spectra of the isolated 1:1 and 1:2 adducts indicated $[A_H\cdot]/[A_D\cdot]$ equal to 5.8 and 6.3, respectively. (Analysis was based on the relative intensity of the ions corresponding to $(CH_3)_2COH^+$ and $(CD_3)_2COH^+$.)

It might therefore be expected that the reaction rates of the following would be equal since $[A_H\cdot]/[A_D\cdot] \cong 6$ and $k_D/k_H \cong 1/6$.

$$A_H\cdot + A_DD \xrightarrow{k_D} A_HD + A_D\cdot$$

$$A_D\cdot + A_HH \xrightarrow{k_H} A_DH + A_H\cdot$$

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(15) J. G. Burr, *J. Phys. Chem.*, **61**, 1477 (1957).

(16) W. H. Urry, Abstracts, 12th National Organic Symposium; Denver, Colo., June, 1951, p. 30.

Since A_DH is formed by several reactions besides the abstraction reaction, its yield is considerably the larger. Therefore, only the yield of A_HD, which is formed only by the abstraction reaction, can be used as a measure of the formation of AM_0B. Statistical and isotope-effect considerations lead to a total G_{AM_0B} of eight times that for G_{A_HD}. Therefore, the G_{A_HD} of 0.2 in the high dose rate experiment leads to a G_{AM_0B} of 1.6. This is an unrealistically high upper limit because the analytical sensitivity required such a high dose that only 3% of the butene remained unreacted; this means that the rate of the propagation reaction is quite diminished during much of the reaction, so that the yield of AM_0B should be enhanced. The true G_{AM_0B} is probably less than unity.

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Mechanisms of Photochemical Reactions in Solution. XXVIII.[1] Values of Triplet Excitation Energies of Selected Sensitizers

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The triplet excitation energies of a number of compounds have been determined by emission spectroscopy. Some of the principles involved in the choice of photosensitizers are discussed.

Introduction

Intermolecular transfer of electronic energy has become a powerful tool for uncovering new photochemical reactions,[3] for directing the course of photochemical reactions,[4] for elucidating the mechanisms of photochemical reactions,[5] and for obtaining information about molecular excited states not possible to obtain by ordinary spectroscopic methods.[6] Transfer of triplet excitation energy,[7] generally more efficient than transfer of singlet excitation in solution, has found extensive application in photochemical reactions. Of special interest are recent studies in this laboratory which have demonstrated a strong dependence of the reaction course upon the triplet excitation energy of the sensitizer (donor).[8,9] For these studies it was necessary to have available a series of sensitizers with triplet excitation energies distributed over a large range.

Only a limited number of triplet state energies have been reported in the literature and, for the most part, the values reported were not satisfactory for our use, either because of discrepancies among these values or because the solvents employed in these determinations differed from those in our experiments. Solvent effects on triplet energy levels depend upon the nature of the transition involved, and significant spectral shifts have been observed. Almost without exception, the literature values were determined with the compounds dissolved in rigid alcohol-containing solvents. The correlation of our results with these reported values was not possible since nonpolar hydrocarbon solvents were employed in our experiments.

We report herein the triplet-state energy values of a large number of compounds, mostly hydrocarbon and carbonyl compounds, as determined from phosphorescence spectra in rigid hydrocarbon solvents at 77°K.

Experimental

The triplet-state energies reported here, unless stated otherwise, were determined from phosphorescence spectra of the compounds dissolved in rigid glasses at 77°K. These spectra were recorded by either of the two methods described below.

Spectrographic Method.—Light from a General Electric AH-4 mercury lamp was filtered through a Corning 7-54 glass color filter and focused on a frozen, degassed solution of the sample contained in a sealed Pyrex tube held in a Pyrex dewar containing liquid nitrogen. The phosphorescence emission, separated from source emission and sample fluorescence by means of a Becquerel phosphoroscope, was focused on the entrance slit of a Bausch and Lomb 0.5-m. quartz prism spectrograph and the spectrum photographed on glass spectroscopic plates. Microdensitometer tracings (Joyce-Loebl recording microdensitometer) were recorded directly from the plates. Mercury lines photographed along with the sample phosphorescence were used to calibrate the spectra.

Spectrophotometric Method.—A photoelectric spectrophosphorimeter consisting of a Jarrell-Ash Ebert scanning monochrometer (*f*/9), an EMI 9558 photomultiplier tube, a "rotating can" phosphoroscope, an electrometer amplifier, and a Bristol 1-sec. strip chart recorder was used to record the spectrum of the phosphorescence emission. The samples were frozen, degassed solutions contained in sealed Pyrex tubes held in a Pyrex dewar containing liquid nitrogen. A G.E. AH-4 source was employed along with interference filters or Corning color glass filters to isolate the groups of mercury lines centered at 3130 and 3660 Å. The spectra were scanned at a rate of 50 Å. per min. A correlation of scanning rate and recorder chart speed allowed wave length determination (±5 Å.) directly from the recorded spectra. The wave length indicator on the monochrometer was calibrated from time to time using the mercury lines as standards. Spectra recorded in this manner were better resolved than those obtained by the photographic method and more accurate determinations of the wave lengths of band maxima could be made.

Solvents.—A variety of solvents or solvent mixtures will form clear glasses when cooled to liquid nitrogen temperatures.[10] Those used in these determinations were 3-methylpentane (MP); methylcyclohexane–isopentane 5:1 by volume (MCIP); isopentane–methylcyclohexane 1:5 (IPMC); ether–isopentane–ethanol 5:5:2 (EPA); and ether–ethanol 1:2 (EA). The hydrocarbon solvents were distilled prior to use. All solvents and solvent mixtures were checked for impurity emission before use.

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(1) Part XXVII: R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).

(2) National Science Foundation Predoctoral Fellow, 1961–present.

(3) See G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(4) See G. S. Hammond, C. A. Stout, and A. A. Lamola, *ibid.*, **86**, 3103 (1964).

(5) See F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

(6) See G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

(7) (a) See G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961); (b) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

(8) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(9) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

(10) (a) W. J. Potts, Jr., *J. Chem. Phys.*, **21**, 191 (1953); (b) K. Rosengren, *Acta Chem. Scand.*, **16**, 1421 (1962).