BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 719—723 (1967)

The Addition Reactions of Ethanol to Ethylene Induced by Gamma-ray Irradiation in the Gaseous Phase. II. A Kinetic Analysis of the Results

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(Received July 4, 1966)

In order to analyze the results obtained in Part I (H. Hotta and H. Kurihara, *Bull. Chem. Soc. Japan*, **40**, 714 (1967)), a general kinetic expression for the system which involves side chain reactions is derived by a modification of the Gale and Wagner method (*J. Am. Chem. Soc.*, **86**, 4531 (1964)) on the basis of the *G*-values without the steady-state approximation. By the use of this expression, the chain transfer constants are found to be $C_1'=0.093$ and $C_2'=0.074$ in the gaseous phase, and about $C_1'=0.007$ in the liquid phase. These values are compared with the reported chain transfer constants for related systems.

The addition reaction of ethanol to ethylene induced by gamma-ray irradiation was studied at a concentration of about 0.11 mol/*l* between 100°C and 200°C, as has been mentioned in Part I.[1)] This reaction in the gaseous phase gives not only 2-alkanols, but also 2-ketones and *t*-alcohols, as a result of the intramolecular hydrogen transfer of the precursor radical of 2-alkanols. Although not all the products expected from the reaction scheme could be detected due to the experimental difficulty, the results obtained in Part I[1)] suggest that the major part of the reaction scheme can be assumed to be as shown in Fig. 1, where AH and E represent ethanol and ethylene respectively. H represents a hydrogen atom of the α-position in an ethanol molecule. Other symbols of the products and intermediate radicals are shown together in Fig. 1.

It is assumed in Fig. 1 that $AE_n\cdot$ radicals react either with ethylene to give $AE_{n+1}\cdot$ (propagation reaction p), or with ethanol to give 2-alkanols, AE_nH and $A\cdot$ (reaction a), or that they are partially rearranged to $AE_n'\cdot$ (reaction r). The rates of these reactions are generally expressed as;

$$p_n = k_{pn}(E)(AE_n\cdot) \tag{1}$$

$$a_n = k_{an}(AH)(AE_n\cdot) \tag{2}$$

$$r_n = k_{rn}(AE_n\cdot) \tag{3}$$

and their total yield is defined as;

$$z_n = p_n + a_n + r_n \tag{4}$$

The *k*'s are rate constants of the respective reactions. Furthermore, it is assumed that the rearranged radicals $AE_n\cdot$ give, by the reaction with ethylene, another type of adducts, $AE_n'E\cdot$ (side chain reaction s), or 2-ketones $KE_n\cdot$ and ethyl radical $HE\cdot$ (reaction d), and that they also give, by the reaction with ethanol, 2-alkanols AE_nH and the starting radical $A\cdot$ (reaction b), and that a part of the $AE_n'E\cdot$ yields *t*-alcohols (reaction t). The rates of these reactions are also expressed as;

$$s_{nm} = k_{snm}(E)(AE_n'E_m\cdot) \tag{5}$$

$$d_n = k_{dn}(E)(AE_n'\cdot) \tag{6}$$

$$b_n = k_{bn}(AH)(AE_n'\cdot) \tag{7}$$

$$t_{nm} = k_{tnm}(AH)(AE_n'E_m\cdot) \tag{8}$$

and

$$r_n = s_{n0} + d_n + b_n \tag{9}$$

Some radicals may become stable products, for example, diols, through radical-radical reactions (termination reaction). However, such termination reactions are neglected due to the low dose rate[2] (1.0×10^5 R/hr[1)]) in the present scheme.

This reaction scheme is rather complex as compared with that of reactions for the 2-propanol - ethylene system, which has only a main propagation reaction.[2,3)] Therefore, the kinetic expression proposed for such a simple system by Gale and Wagner[2)] must be modified to include side reactions for the sake of the analysis of the ethanol-ethylene system. The characteristic of the present method is that the expression is derived on the basis of *G*-values, without the steady-state approximation.

General Kinetic Expression

When the initial *G*-value of the $A\cdot$ radical, formed primarily by irradiation, is put as G_{A1},

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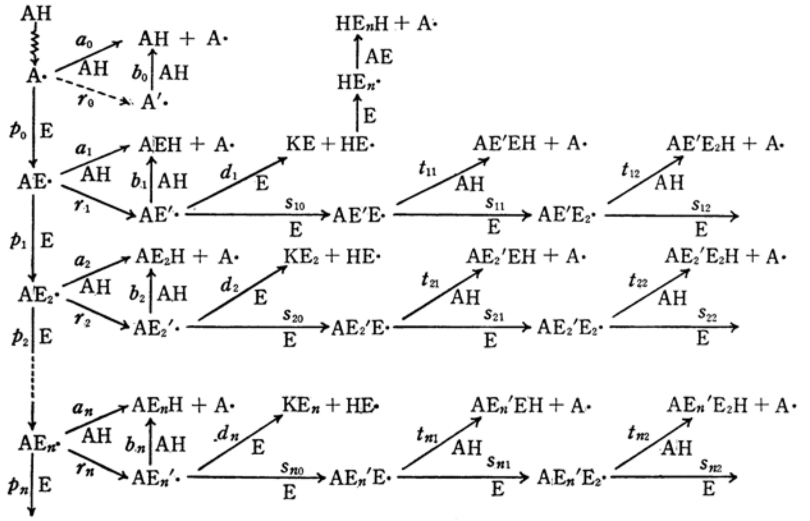
1) H. Hotta, H. Kurihara and T. Abe, This Bulletin, **40**, 712 (1967).

2) L. H. Gale and C. D. Wagner, *J. Am. Chem. Soc.*, **86**, 4531 (1964).

3) T. Kurihara and H. Hotta, This Bulletin, **37**, 1448 (1964).



Notation:

AH	$\mathrm{CH_3CH_2OH}$	$\mathrm{AE}_n{}'\cdot$	$\mathrm{CH_3\dot{C}OH(CH_2CH_2)}_n\mathrm{H}$
A·	$\mathrm{CH_3\dot{C}HOH}$	$\mathrm{AE}_n{}'\mathrm{E}_m\cdot$	$\cdot(\mathrm{CH_2CH_2})_m\underset{\substack{\mid\\ \mathrm{CH_3}}}{\mathrm{C}}\mathrm{OH}(\mathrm{CH_2CH_2})_n\mathrm{H}$
E	$\mathrm{CH_2CH_2}$	$\mathrm{AE}_n{}'\mathrm{E}_m\mathrm{H}$	$\mathrm{H}(\mathrm{CH_2CH_2})_m\underset{\substack{\mid\\ \mathrm{CH_3}}}{\mathrm{C}}\mathrm{OH}(\mathrm{CH_2CH_2})_n\mathrm{H}$
$\mathrm{AE}_n\cdot$	$\mathrm{CH_3CHOH(CH_2CH_2)}_n\cdot$	$\mathrm{HE}_n\cdot$	$\mathrm{H(CH_2CH_2)}_n\cdot$
$\mathrm{AE}_n\mathrm{H}$	$\mathrm{CH_3CHOH(CH_2CH_2)}_n\mathrm{H}$	$\mathrm{HE}_n\mathrm{H}$	$\mathrm{H(CH_2CH_2)}_n\mathrm{H}$
KE_n	$\mathrm{CH_3C({=}O)(CH_2CH_2)}_n\mathrm{H}$		

Fig. 1. The whole reaction scheme.

the yield of the regeneration of this radical is expressed, from the scheme in Fig. 1, as;

$$G(\mathrm{A}\cdot)_1 = \frac{a_0 + b_0}{p_0 + a_0 + r_0} \times G_{\mathrm{A1}}$$
$$= \frac{a_0 + b_0}{z_0} \times G_{\mathrm{A1}}$$

but $r_n=0$ for $n=0$. The yield of the AE· radical by this process is similarly given by

$$G(\mathrm{AE}\cdot) = (p_0/z_0) \times G_{\mathrm{A1}}$$

Successively, the yields of 2-alkanols, $\mathrm{AE}_n\mathrm{H}$, from the first-formed A· radical are given by;

$$G(\mathrm{AEH})_1 = (a_1 + b_1)/(z_1) \times G(\mathrm{AE}\cdot)_1$$
$$= (a_1 + b_1)p_0/(z_1 z_0) \times G_{\mathrm{A1}}$$
$$G(\mathrm{AE_2H})_1 = (a_2 + b_2)(p_1 p_0)/(z_2 z_1 z_0) \times G_{\mathrm{A1}}$$
$$\vdots$$
$$G(\mathrm{AE}_n\mathrm{H})_1 = \frac{a_n + b_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \times G_{\mathrm{A1}}$$

Similarly, since $d_n/z_n=(r_n/z_n)(d_n/r_n)$, the yield of 2-ketones, KE_n, and *t*-alcohols, $\mathrm{AE}_n{}'\mathrm{E}_m\mathrm{H}$, are given, respectively, in the forms;

$$G(\mathrm{KE}_n)_1 = \frac{d_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \times G_{\mathrm{A1}}$$

and

$$G(\mathrm{AE}_n{}'\mathrm{E}_m\mathrm{H})_1 = \frac{t_{nm}}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \times G_{\mathrm{A1}}$$

The A· radicals are also regenerated from these successive reactions, as is shown in Fig. 1. Therefore, the over-all yield of this radical, starting from the primary A·, is given by;

$$G_{\mathrm{A2}} = \sum_{n=0}^{\infty} G(\mathrm{AE}_n\mathrm{H}) + \sum_{n=0}^{\infty} G(\mathrm{KE}_n)$$
$$+ \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} G(\mathrm{AE}_n{}'\mathrm{E}_m\mathrm{H})$$

This equation is expressed by G_{A1} as;

$$G_{\mathrm{A2}} = fG_{\mathrm{A1}}$$

where

$$f = \sum_{n=0}^{\infty} \frac{a_n + r_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} - x$$

(x=correction for termination loss neglected in the scheme)

The regenerated A· radicals react also in a similar way, as do also regenerate the A· radicals. The yields of the products, formed from the first regenerated A· radicals (G_{A2}) during the second cycle, are given by a similar expression, for example,

$$G(\mathrm{AE}_n\mathrm{H})_2 = \frac{a_n + b_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \times G_{\mathrm{A2}}$$

$$= \frac{a_n + b_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \times f G_{A1}$$

The A· radicals, regenerated during the second cycle (G_{A3}) start the third cycle.

Since the regeneration coefficients, *f*, are equal for each cycle, the total yields of the products are given as the sum of the yield formed during each cycle in the following forms;

$$\begin{aligned} G(AE_nH) &= \frac{a_n + b_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \\ &\quad \times (1 + f + f^2 \cdots + f^{n-1}) \times G_{A1} \\ &= \frac{a_n + b_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \left(\frac{1}{1-f}\right) G_{A1} \qquad (10) \end{aligned}$$

$$G(KE_n) = \frac{d_n}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \left(\frac{1}{1-f}\right) G_{A1} \qquad (11)$$

and

$$G(AE_n'E_mH) = \frac{t_{nm}}{z_n} \prod_{i=0}^{n-1} \frac{p_i}{z_i} \left(\frac{1}{1-f}\right) G_{A1} \qquad (12)$$

for $-1 < f < 1$.

Chain Transfer Constants

From Eq. (10), the ratio of $G(AE_nH)/G(AE_{n+1}H)$ is;

$$\begin{aligned} \frac{G(AE_nH)}{G(AE_{n+1}H)} &= \frac{(a_n + b_n) z_{n+1}}{(a_{n+1} + b_{n+1}) p_n} \\ &= \frac{a_n'}{p_n}\left(1 + \frac{r_{n+1}'}{a_{n+1}'}\right) + \left(\frac{a_n'}{p_n}\right) \Big/ \left(\frac{a_{n+1}'}{p_{n+1}}\right) \qquad (13) \end{aligned}$$

using Eq (4), where $a_n' = a_n + b_n$ and $r_n' = r_n - b_n$.

Although the true chain transfer constant is;

$$C_n = \frac{k_{an}}{k_{pn}} = \frac{a_n}{p_n} \times \frac{1}{R} \qquad (14)$$

where $R = (AH)/(E)$, the apparent chain transfer constant is now defined as;

$$C_n' = \frac{a_n'}{p_n} \times \frac{1}{R} = C_n + \frac{k_{bn}(AE_n'\cdot)}{k_{pn}(AE_n\cdot)} \qquad (15)$$

Substituting Eq. (15) in Eq. (13), the ratio is rewritten as;

$$\begin{aligned} \frac{G(AE_nH)}{G(AE_{n+1}H)} &= C_n'R\left(1 + \frac{r_{n+1}'}{a_{n+1}'}\right) + \frac{C_n'}{C_{n+1}'} \\ &= C_n'R\left(1 + \frac{G(KE_{n+1}) + \sum_{m=1}^{\infty} G(AE_{n+1}'E_mH)}{G(AE_{n+1}H)}\right) \\ &\quad + \frac{C_n'}{C_{n+1}'} \qquad (16) \end{aligned}$$

Then, the apparent chain transfer constants, C_n' and C_{n+1}', are obtained by substituting the observed *G*-values of the respective products into Eq. (16).

For $n=1$, Eq. (16) is rewritten as

$$\begin{aligned} \frac{G(AEH)}{G(AE_2H)} &= C_1'R\left(1 + \frac{\left(\begin{array}{c} G(KE_2) + G(AE_2'EH) \\ + G(AE_2'E_2H) + \cdots \end{array}\right)}{G(AE_2H)}\right) \\ &\quad + \frac{C_1'}{C_2'} \qquad (17) \end{aligned}$$

The chain transfer constants for the gaseous mixture of 2-propanol and ethylene are $C_1 = 0.62$, $C_2 = 0.55$, and $C_3 = 0.50$ under almost the same condition as in the present study (Part I).1,3) Therefore, if the same chain transfer constants can be assumed for the side propagation reaction, s_n, of the present system ($n=1$ or 2), the following relationships are obtained in spite of the imperfect detection of *t*-alcohols, that is,

$$k_{t11}/k_{s11} = k_{t21}/k_{s21} = 0.62 \qquad (18)$$

$$k_{t12}/k_{s12} = k_{t22}/k_{s22} = 0.55 \qquad (19)$$

and

$$k_{t13}/k_{s13} = k_{t23}/k_{s23} = 0.50 \qquad (20)$$

Since the fraction of $AE_n'E\cdot$, which yields $AE_n'EH$, is

$$\frac{t_{n1}}{s_{n1} + t_{n1}} = \frac{0.62R}{1 + 0.62R}$$

from Eq. (18), the yield of $AE_n'EH$ is given by;

$$G(AE_n'EH) = \left(\frac{0.62R}{1 + 0.62R}\right) G(AE_n'E\cdot)$$

The yields of *t*-alcohols are obtained successively as;

$$\begin{aligned} G(AE_n'E_2H) &= \left(\frac{1}{1 + 0.62R}\right) \\ &\quad \times \left(\frac{0.55R}{1 + 0.55R}\right) G(AE_n'E\cdot) \end{aligned}$$

and

$$\begin{aligned} G(AE_n'E_3H) &= \left(\frac{1}{1 + 0.62R}\right)\left(\frac{1}{1 + 0.55R}\right) \\ &\quad \times \left(\frac{0.50R}{1 + 0.50R}\right) G(AE_n'E\cdot) \end{aligned}$$

from Eqs. (19) and (20). Therefore, the ratios between the yields of *t*-alcohols in Eq. (17) are obtained as;

$$\frac{G(AE_n'E_2H)}{G(AE_n'EH)} = \frac{0.887}{1 + 0.55R} \qquad (21)$$

and

$$\frac{G(AE_n'E_3H)}{G(AE_n'EH)} = \frac{0.806}{(1 + 0.55R)(1 + 0.50R)} \qquad (22)$$

These relationships are applicable with a good accuracy for $n=1$ or 2.

The yields of 3-methyl-3-pentanol ($AE'EH$) and 3-methyl-3-heptanol ($AE'E_2H + AE_2'EH$) are determined from the experiments in Part I.1) By substituting these values into Eqs. (21) and

TABLE 1. CALCULATED YIELDS OF *t*-ALCOHOLS

R	$G(AE'EH)$	$G(AE'E_2H)$	$G(AE'E_3H)$	$G(AE_2'EH)$	$G(AE_2'E_2H)$	$G(AE_2'E_3H)$
8.52	4.6	0.7	0.1	12.5	2.0	0.3
3.13	6.9	2.2	0.8	18.7	6.1	2.2
2.31	8.4	3.3	1.4	25.3	9.9	4.2
1.92	8.8	3.8	1.8	29.5	12.7	5.9
1.00	2.9	1.7	1.0	4.8	2.8	1.7

(22), the yields of *t*-alcohols, $AE'EH$, $AE'E_2H$, $AE'E_3H$, $AE_2'EH$, $AE_2'E_2H$, and $AE_2'E_3H$, are estimated to be as shown in Table 1. In Table 1, the $G(AE_2'EH)$, obtained semi-empirically with the aid of Eq. (21), are larger than the observed $G(AE'EH)$.

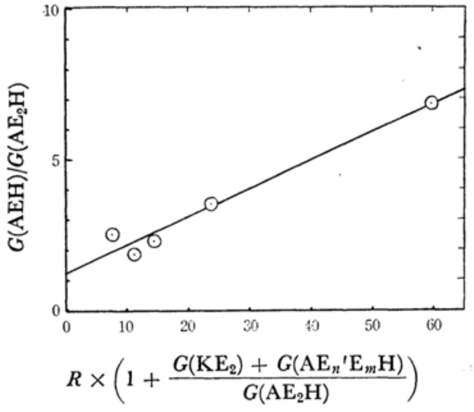


Fig. 2. Plot for determination of apparent chain transfer constants from Eq. (17).

TABLE 2. CHAIN TRANSFER CONSTANT FOR ALCOHOL-ETHYLENE SYSTEMS

Alcohol	Phase	Temp. °C	Chain transfer constant
Methanol	Gas	—	—
	Liquid[4]	100	0.006
Ethanol	Gas	175	$C_1'=0.093$
			$C_2'=0.074$
	Liquid	100	$C_1'\leq 0.007$
	Liquid[5]	130	0.019
2-Propanol	Gas[3]	175	$C_1=0.62$
			$C_2=0.55$
			$C_3=0.50$
	Liquid[6]	—	$C_1=0.062$
			$C_2=0.056$
			$C_3=0.073$

The ratios of $G(AEH)/(G(AE_2H)$ are plotted in Fig. 2 against $R\times[1+(G(KE_2)+G(AE_2'EH)+G(AE_2'E_2H)+G(AE_2'E_3H))/G(AE_2H)]$, using the values in Table 1. Then, the apparent chain transfer constants, $C_1'=0.093$ and $C_2'=0.074$, are obtained from Fig. 2 on the basis of Eq. (17). These values are listed along with the values for the related systems, in Table 2.[4-6] Addition reactions for these systems are initiated by gamma-rays, except the reactions initiated by peroxides.[5] The value in Table 2 is larger for 2-propanol than for ethanol. Since, according to Trotman-Dickenson *et al.*,[7] the rate of the hydrogen abstraction by the methyl radical is 1.0×10^{-5} mol^{-1}cm^{3}sec^{-1} for ethanol, and 3.1×10^{-5} mol^{-1}cm^{3}sec^{-1} for 2-propanol, this difference is due to the rate of the hydrogen abstraction. The value is also larger for the gaseous system than for the liquid system. However, this may be due not only to the phase, but also to either the low mole fraction of ethylene or the lower reaction temperature, as has been pointed out in Part I.[1]

If the reactions in the liquid phase give only the products in Table 7 of Part I,[1] Eq. (17) is simplified as;

$$\frac{G(AEH)}{G(AE_2H)}=C_1'R\left(1+\frac{G(AE_2'EH)}{G(AE_2H)}\right)+\frac{C_1'}{C_2'}\quad(23)$$

When the C_1'/C_2' ratio is assumed to be between 1.5 and 0.5, a C_1' value between 0.0055 and 0.0074 is obtained on substituting the observed G-values into Eq. (23). This is rather smaller than the value reported in Table 2.[5]

The Rate of Respective Reactions. The values of a_1'/p_1 and a_2'/p_2 are obtained from Eq. (15) by using the above apparent chain transfer constants. The values of a_1'/d_1 and a_2'/d_2 are also obtained as the ratio of the observed G(2-alkanol) value to the G(2-ketone). Similarly, the values of s_{10}/d_1 and s_{20}/d_2 are obtained from the G-values in Table 1 by using the relationship for $n=1$ and 2;

$$\frac{\sum_{n=1}^{\infty}G(AE_n'E_mH)}{G(KE_n)}=\frac{s_{n0}}{d_n}=\frac{k_{sn0}}{k_{dn}}\quad(24)$$

These values are listed in Table 3. The ratios,

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4) M. Takehisa, M. Yasumoto and Y. Urano, private communication.

5) W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).

6) K. Hirota and M. Hatada, This Bulletin, **34**, 1644 (1961).

7) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

s_{10}/d_1 and s_{20}/d_2, representing k_{s10}/k_{d1} and k_{s20}/k_{d2} from Eq. (24) are almost constant over the whole range of R in Table 3. The k_{s10}/k_{d1} is 0.49±0.04, and the k_{s20}/k_{d2} is 1.03±0.07. It is noted that the former is a half of the latter.

TABLE 3. RATE RATIOS

R	a_1/p_1	a_1'/d_1	s_{10}/d_1	a_2'/p_2	a_2'/d_2	s_{20}/d_2
8.52	0.79	4.00	0.57	0.63	0.30	0.81
3.13	0.29	1.23	0.41	0.23	0.30	0.98
2.31	0.21	0.99	0.40	0.17	0.42	1.18
1.92	0.18	0.82	0.69	0.14	0.50	1.37
1.00	0.09	0.58	0.40	0.07	0.27	0.81

Since all the G-values in Part I[1] are estimated on the assumption that even the energy absorbed by ethylene is dissipated chemically after being transferred to ethanol, the amount of the A· radical formed primarily should be independent of the composition of the mixture. Therefore, in Eq. (1), p_θ is proportional to the concentration of ethylene. Since an ethanol molecule does not always combine with only one ethylene molecule, the amount of ethylene consumed does not directly represent p_0. On the other hand, this amount is proportional to the mole fraction of ethylene, as seen in Fig. 1 of Part I.[1] This means that this amount can be used as a substitute for p_0. Therefore, when the $G(-C_2H_4)$ observed is divided into parts by using the ratios in Table 3, each part represents the relative fraction of the respective reactions in Fig. 1. Such fractions are plotted as a function of R in Figs. 3 and 4.

It may be noted that the rates s_{20} and d_2 in Fig. 4 are much larger than the rates s_{10} and d_1 in Fig. 3, and that the sum of s_{20} and d_2 is much larger than the sum of p_2 and a_2' in Fig. 4. This indicates that the intramolecular rearrangement for $AE_n'\cdot$ is much preferable for $n=2$, as has been pointed out in Part I.[1] In spite of the large s_{20} and d_2 values, the a_2' rate is so small that the b_2 rate may be supposed to be also very small. Therefore, the second term in Eq. (15) can be neglected. This means that the apparent chain transfer constant, C', approximately represents the true constant, C (Eq. (14)).

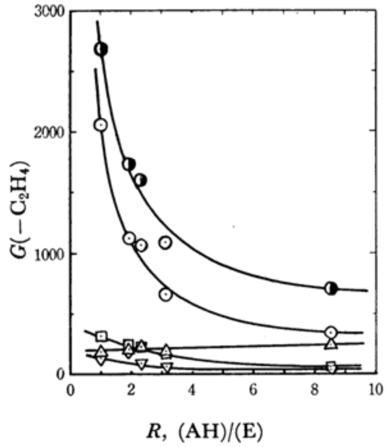

Fig. 3. Calculated rates of respective reactions for $n=1$, represented by $G(-C_2H_4)$: p_0 (◑), p_1 (⊙), a_1' (◬), d_1 (⊡) and s_{10} (▽).

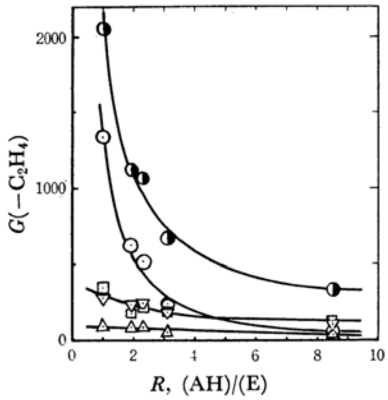

Fig. 4. Calculated rates of respective reactions for $n=2$, represented by $G(-C_2H_4)$: p_1 (◑), p_2 (⊙), a_2' (◬), d_2 (⊡) and s_{20} (▽).