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Correlations of the Structural Unit of Organic Compounds with the *G* Values of Thier Radiolytic Products

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Two correlations have been found between the G values of the radiolytic products and the number of the structural unit, n, in an organic molecule; (i) The G value from the homologous compounds has a linear relation to $1/n$ in the $n \leqq m$ region and is independent of n in the $n \geqq m$ region, where m is the number of the C–C bond through which the energy can be transferred, and (ii) the $G(CH_4)$ value from paraffin hydrocarbons, where the "terminal effect" is remarkable, has a linear relation to $1/n$ in both the $n \geqq m$ and $n \leqq m$ regions. These relations may be explained in terms of the energy transfer through C–C bonds.

Many studies have been carried out of radiation effects on chemical substances, but fewer investigations into correlations of the radiation effect on substances with their chemical structures have been made.[1-4]

In a previous paper,[5] the radiolysis of ethylene glycol diacetate was studied in order to investigate the effect of the number of ester groups in a molecule; it was found that the yields of gaseous products from ethylene glycol diacetate range from a half to one-third of those from methyl acetate. In the present paper, a similar method of research has been extended to other series of compounds in order to obtain a general rule which can predict the radiation effect for related compounds. Such research may also be useful for a better understanding of the mechanisms of the radiation effect on chemical substances in general.

Experimental

Commercially-available triacetin, glycerol, erythritol, and acetonylacetone were used without further purification.

In each run, each sample (2 ml., or 2 g. in the case of erythritol) was degassed by a conventional vacuum technique in a glass ampoule equipped with a breakable seal. Then the ampoule was sealed off and subjected to irradiation at room temperature with cobalt-60 gamma rays. The dose rate, which was determined by the use of a Fricke ferrous sulfate dosimeter, was 3.1×10^{15} eV. g^{-1} sec^{-1}.

The gaseous products were collected with a Toepler pump through traps at −196°C and −78°C; after their

TABLE I. *G* VALUES FROM IRRADIATED $-(-CHOOCCH_3-)-_n$

Compound	n	Radiation	Temp. °C	Phase	$G(H_2)$	$G(CH_4)$	$G(C_2H_6)$	$G(CO)$	$G(CO_2)$	Ref.
CH_3OOCCH_3	1	γ	R.T.	l.	0.87	2.07	0.27	1.57	0.78	6
	1	γ	27	l.	0.76	2.03	0.34	1.64	0.95	7
CH_2OOCCH_3 $\vert$ CH_2OOCCH_3	2	γ	R.T.	l.	0.34	0.70	0.10	0.76	0.28	5
CH_2OOCCH_3 $\vert$ $CHOOCCH_3$ $\vert$ CH_2OOCCH_3	3	γ	R.T.	l.	0.11	0.27	0.05	0.46	0.26	This work

R.T.: Room temperature l.: liquid

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amounts had been determined, they were subjected to mass spectrometry.

Results and Discussion

This general formula of the compounds can be presented: $-(-CHR-)-_n$; that is, $n=1$: CH_3R, $n=2$: CH_2RCH_2R, $n=3$: $CH_2RCHRCH_2R$,...... Tables I—IV show the *G* values of products from a series of esters ($R=CH_3COO$), alcohols ($R=HO$), ketones ($R=CH_3CO$), and paraffin hydrocarbons ($R=H$) respectively. In the tables, the *G* values of products from four irradiated compounds (tri-

TABLE II. *G* VALUES FROM IRRADIATED $-(-CHOH-)-_n$

Compound	n	Radiation	Temp. °C	Phase	$G(H_2)$	$G(CH_4)$	$G(CO)$	Ref.
CH_3OH	1	γ	R.T.	l.	4.0	0.24	0.16	8
	1	γ		l.	5.39	0.11	0.54	9
	1	γ		l.	4.1	1.23	0.15	10
	1	γ	20—25	l.	4.57	(0.36)*		11
	1	γ	19	l.	5.40	0.80	0.15	12
	1	γ	26	l.	5.66	0.57	0.45	13
	1	γ	20	l.	4.1	0.39	0.13	14
	1	γ		l.	4.99	0.44	0.12	15
	1	γ	20	l.	4.98	0.28	0.09	16
	1	γ	20	l.	4.60	0.31	0.15	16
	1	γ	22	g.	10.4	0.26	0.84	17
	1	γ	40—42	g.	10	0.5	1.0	18
CH_2OH | CH_2OH	2	γ	R.T.	l.	1.9	0.097	0.015	19
CH_2OH | $CHOH$ | CH_2OH	3	γ	R.T.	l.	1.8	0.002	0.034	This work
CH_2OH | $CHOH$ | $CHOH$ | CH_2OH	4	γ	R.T.	s.	1.1	0.000	0.000	This work

R.T.: Room temperature g.: gas l.: liquid s.: solid * $G(CH_4)+G(CO)$

TABLE III. *G* VALUES FROM IRRADIATED $-(-CHCOCH_3-)-_n$

Compound	n	Radiation	Temp. °C	Phase	$G(H_2)$	$G(CH_4)$	$G(CO)$	$G(C_2H_6)$	Ref.
CH_3COCH_3	1	γ	27	l.	0.88	2.62	0.83	0.48	20
	1	γ		l.	0.84	1.9	0.63	—	21
	1	γ	17	l.	0.85	1.84	1.70	0.43	22
	1	γ	28	l.	0.54	2.00	0.75	0.29	23
CH_2COCH_3 | CH_2COCH_3	2	γ	R.T.	l.	0.24	0.27	0.25	0.22	This work

R.T.: Room temperature l.: liquid

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TABLE IV. G VALUES FROM IRRADIATED $-(-\mathrm{CH_2}-)-_n$

Compound	n	Radiation	Temp. °C	Phase	$G(\mathrm{H_2})$	$G(\mathrm{CH_4})$	Ref.
$\mathrm{CH_4}$	1	γ	22.5	g.	6.4		24
	1	α		g.	6.4*		25
	1	e		g.	5.7		26
	1	α		g.	4.8		27
	1	γ	25	g.	5.51		28
	1	x	25	g.	7.2		29
	1	γ	−196	s.	2.87		30
$\mathrm{C_2H_6}$	2	γ	22.5	g.	6.8	0.6	24
	2	α		g.	5.0*	1.0*	25
	2	e	R.T.	g.	3.9	0.49	31
	2	γ	25	g.	8.8	0.39	32
	2	γ	25	g.	8.3	—	33
	2	γ		l.	7.00—8.60	—	34
$\mathrm{C_3H_8}$	3	γ	22.5	g.	5.9	1.5	24
	3	α		g.	8.2	0.37	35
	3	α		g.	4.3*	1.2*	25
	3	γ		g.	6.25	—	36
	3	e	R.T.	g.	—	1.3	37
	3	γ		l.	5.50—7.45	—	34
$\mathrm{C_4H_{10}}$	4	γ	170	g.	4.75—6.12	1.16—2.56	38
	4	α		g.	9.0	1.2	35
	4	α		g.	4.8*	0.89*	25
	4	γ		g.	4.92—5.41	—	34
	4	γ		g.	5.40	—	36
	4	γ	20	l.	4.05—4.50	0.42—0.49	38
	4	e	−30	l.	1.1	0.2	39
$\mathrm{C_5H_{12}}$	5	e		g.	>6	0.7	40
	5	α		g.	7.3	0.81	35
	5	e	22	l.	4.2	0.22	41
	5	e		l.	4.2	0.4	42
	5	γ		l.	4.5	—	43
	5	x		l.	6.35	—	44
	5	e		l.	4.98	0.12	45
	5	γ	25	l.	4.17	0.22	46
	5	γ	R.T.	l.	5.04	0.25	47

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TABLE IV. (Continued)

Compound	n	Radiation	Temp. °C	Phase	$G(H_2)$	$G(CH_4)$	Ref.
C_6H_{14}	6	e		g.	4.3	0.5	48
	6	α		g.	5.6	0.78	35
	6	α		g.	3.5	0.44	51
	6	e	R.T.	g.	5.0	0.5	53
	6	e		l.	4.95	0.13	48
	6	e		l.	5.0	0.15	42
	6	e		l.	5.0	0.41	49
	6	e, γ		l.	4.0	0.12	50
	6	γ		l.	4.9	0.4	52
	6	γ		l.	5.1	—	43
	6	x		l.	5.28	0.11	44
	6	γ	20	l.	5.09	—	54
	6	γ	−196	s.	3.65	—	54
C_7H_{16}	7	e		l.	4.7	0.09	42
	7	e		l.	5.1	0.27	49
	7	γ	9	l.	4.9	0.22	55
	7	x	25—75	l.	5.2	—	56
	7	x		l.	6.06	—	44
C_8H_{18}	8	e		l.	4.8	0.08	42
	8	e		l.	4.7	0.17	49
	8	γ		l.	5.0	—	43
	8	x		l.	6.18	—	44
	8	γ	R.T.	l.	4.59	0.08	47
C_9H_{20}	9	e		l.	5.0	0.07	42
	9	γ		l.	4.9	—	43
	9	x		l.	6.05	—	44
$C_{10}H_{22}$	10	e		l.	5.2	0.06	42
	10	e		l.	4.2	0.11	49
	10	γ		l.	4.8	—	43
	10	x		l.	4.90	—	44
$C_{12}H_{26}$	12	e		l.	4.9	0.05	42
$C_{14}H_{30}$	14	e		l.	4.1	0.07	49
$C_{16}H_{34}$	16	e		l.	4.8	0.04	42
	16	e	19	l.	4.1	—	57
	16	e	4	s.	3.0	—	57
$C_{28}H_{58}$	28	e	25—50	s.	4.3	—	58
Polymethylene	∞	e	25—50	s.	5.4	0	58

* Calculated from author's data, assuming W=26.

R.T.: Room temperature. g.: gas l.: liquid s.: solid

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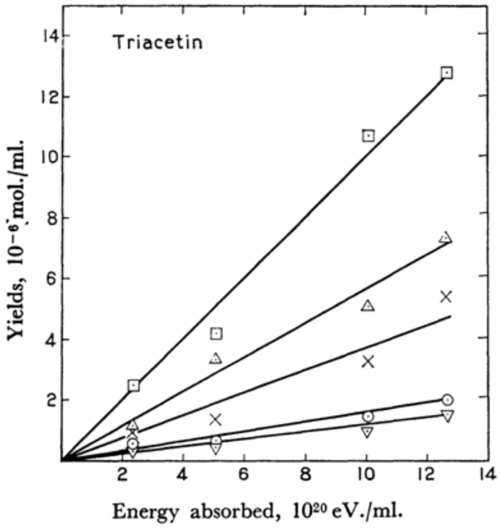

Fig. 1. Yields of gaseous products as a function of energy absorbed.

⊙ H_2, △ CH_4, ⊡ CO, ▽ C_2H_6, × CO_2

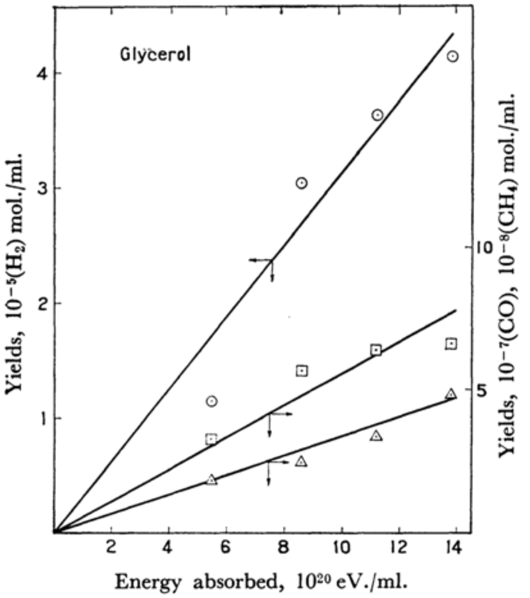

Fig. 2. Yields of geseous products as a function of energy absorbed.

⊙ H_2, △ CH_4, ⊡ CO

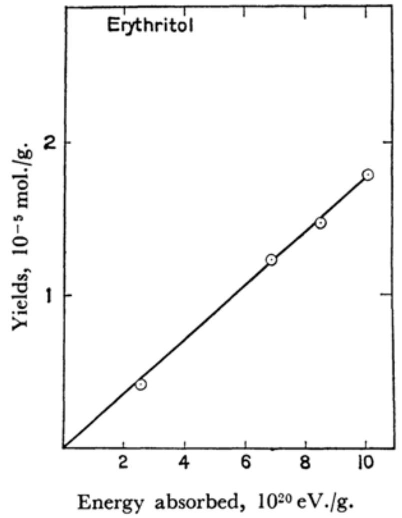

Fig. 3. Yields of hydrogen as a function of energy absorbed.

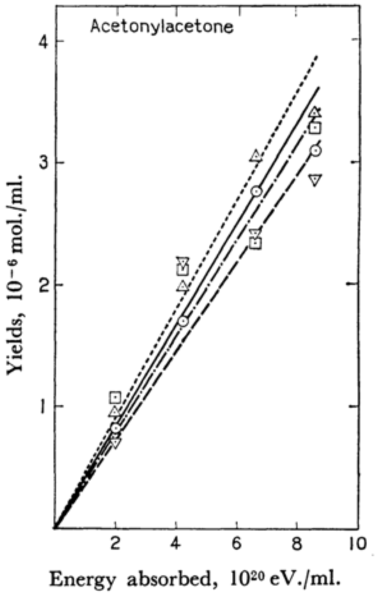

Fig. 4. Yields of gaseous products as a function of energy absorbed.

⊙ H_2, △ CH_4, ⊡ CO, ▽ C_2H_6

acetin, glycerol, erythritol and acetonylacetone) were obtained, as usual, from the straight lines shown in Figs. 1, 2, 3 and 4. The *G* values of the others were obtained from the literature.

The *G* values for gaseous products from various series of compounds are plotted against the reciprocal of the number of the structural unit, $1/n$, in Figs. 5, 6 and 7. When the *G* values obtained from various authors are used for the sake of comparison, the differences in the experimental conditions, such as the types of radiation, the irradiation temperature, the dose rate, the dose, and the density of the samples, should be taken into consideration. Therefore, for the paraffin series, the *G* values which were obtained under the most similar experimental conditions are plotted in Figs. 8 and 9. The *G* values from gaseous substances are plotted in Figs. 8a and 9a, while those from liquid or solid substances are plotted in Figs. 8b and 9b. The *G* values obtained by different authors are

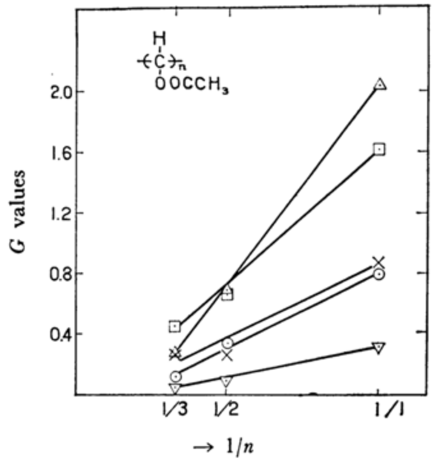

Fig. 5. *G* values vs. reciprocal of the number of the structural unit.

⊙ H_2, △ CH_4, ⊡ CO, ▽ C_2H_6, × CO_2

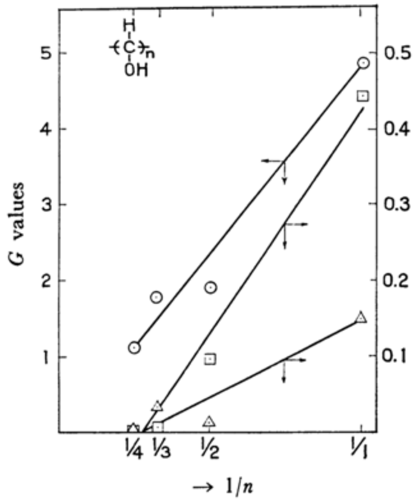

Fig. 6. *G* values vs. reciprocal of the number of the structural unit.

⊙ H_2, △ CH_4, ⊡ CO

also plotted by the use of different symbols in Figs. 8c and 9c. The mean values were adopted as representative when different *G* values have been reported for a compound.

The *G* values have linear relations to the reciprocal of the number of the structural unit, $1/n$, in the $R=CH_3COO$, $R=HO$ and $R=CH_3CO$ series. In the series of paraffin hydrocarbons, $R=H$, $G(H_2)$ is independent of the structural unit in the $n \geqq$ ca. 6 region and has a linear relation to $1/n$ in the $n \leqq$ ca. 6 region as well as *G* values from the other series, while $G(CH_4)$ has an almost linear relation to $1/n$ in the two regions.

A schematic process of this radiation-chemical reaction may be presented as follows. The molecule which absorbs energy from ionizing radiations is excited or ionized:

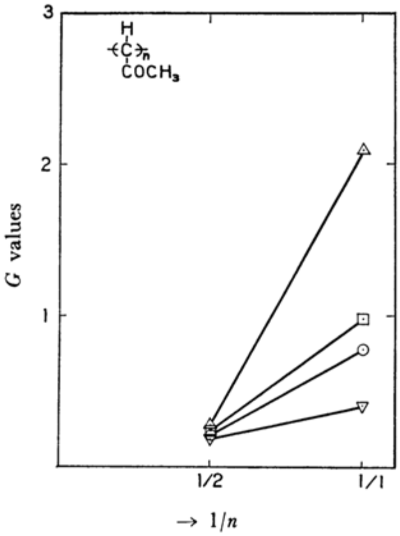

Fig. 7. *G* values vs. reciprocal of the number of the structural unit.

⊙ H_2, △ CH_4, ⊡ CO, ▽ C_2H_6

$$A \rightsquigarrow \left[\begin{array}{l} A^+ + e^- \\ A^* \end{array} \right. \qquad (1)$$

Some produced ions turn finally into excited molecules by means of electron capture;

$$A^+ + e^- \longrightarrow A^* \qquad (2)$$

Therefore the primary species correspond to excited molecules or molecular ions, which decompose into radicals and/or produce stable molecules through recombination, abstraction, disproportionation, and other reactions:

$$A^+, A^* \longrightarrow B + C \qquad (3)$$

In short, a molecule which absorbs energy of radiation is excited or ionized, and these species decompose to radicals and/or stable products by the bond-rupture of the main or side chain. On the other hand, the overall yield of the product thus formed is generally expressed by the *G* value. The above relations between the structural units of the compounds and the *G* values of the products can be explained if the mechanism of the unimolecular decomposition of the excited molecule or molecular ion and the successive reactions are available.

It was proposed by Alexander and Charlesby[59] that the energy absorbed may be transferred over a comparatively far distance along the C–C chain; they based their proposal on their experimental findings that a copolymer of 20 per cent styrene

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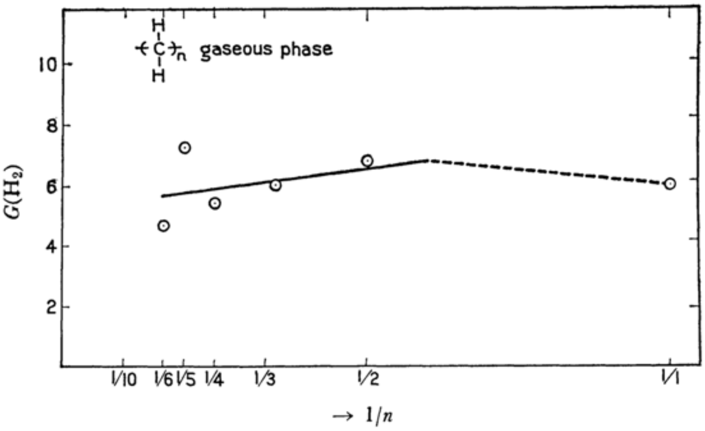

Fig. 8a. *G* values vs. reciprocal of the number of the structural unit.

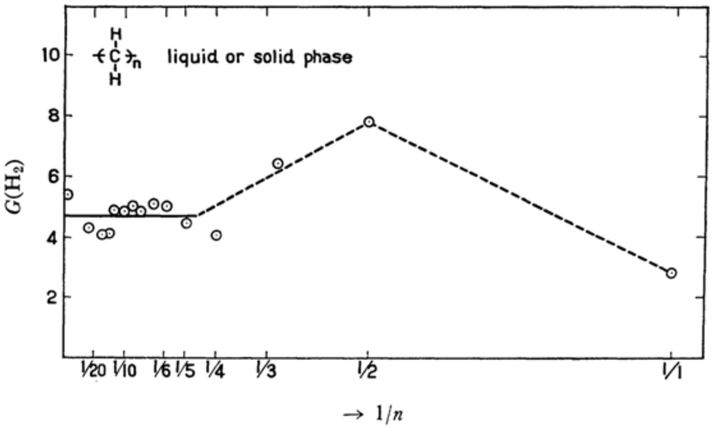

Fig. 8b. *G* values vs. reciprocal of the number of the structural unit.

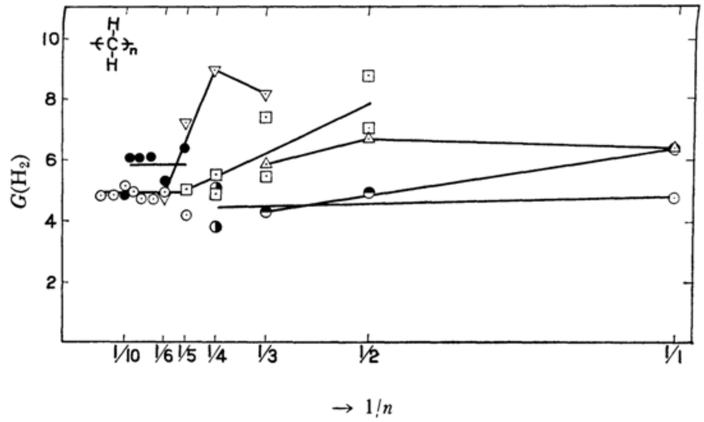

Fig. 8c. *G* values vs. reciprocal of the number of the structural unit.

⊙ Ref. 42, ⊡ Ref. 36, ● Ref. 44, ◓ Ref. 25,
△ Ref. 24, ▽ Ref. 35, ◑ Ref. 27

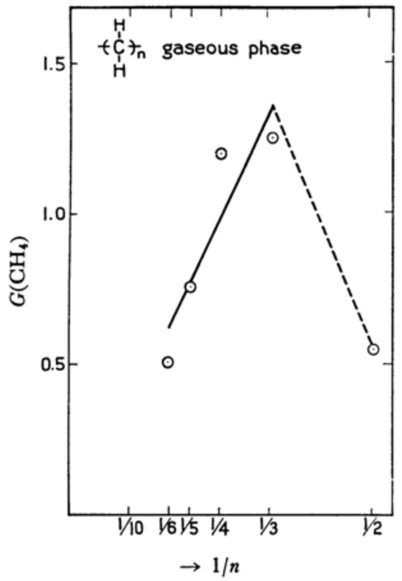

Fig. 9a. *G* values vs. reciprocal of the number of the structural unit.

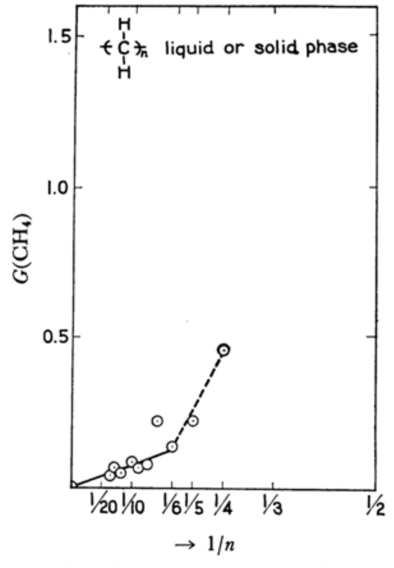

Fig. 9b. *G* values vs. reciprocal of the number of the structural unit.

and 80 per cent isobutylene is more resistant than the pure isobutylene, and that dose required to render a straight-chain hydrocarbon infusible is greatly increased by the presence of an aromatic ring.

It is interesting to compare the results of the following two systems; in one, (A) is a monomer, M, while in the other (B) is a polymer composed of such a monomer, the monomeric unit being assumed to have a similar chemical structure in both systems:

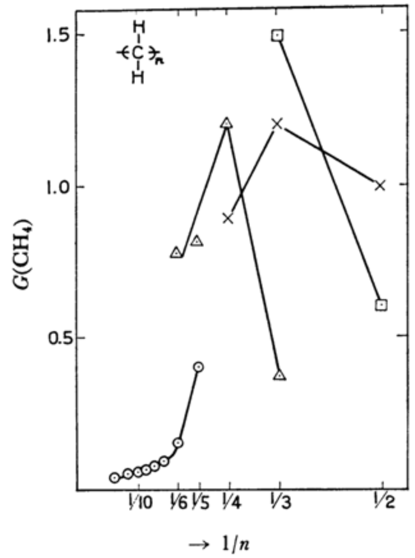

Fig. 9c. *G* values vs. reciprocal of the number of the structural unit.

⊙ Ref. 42, △ Ref. 25, ▣ Ref. 35, × Ref. 24

$$\begin{array}{lccc}
 & M & M & M \\
(A) & M & M^* & M \\
 & M & M & M
\end{array}
\qquad
\begin{array}{lc}
 & -M-M-M \\
(B) & -M-M^*-M- \\
 & -M-M-M-
\end{array}$$

In the A system, the energy absorbed is localized on the excited molecule, M*, and enhances the probability of the decomposition of M*, although some part of the energy may be transferred to other molecules. On the other hand, in the B system, the energy absorbed is transferred away by an intramolecular process through the chemical bonds in addition to the intermolecular process. Therefore, the *G* values of decomposition may be expected to be larger in the A system than in the B system, and if homologous compounds are compared, their *G* values will decrease with an increase in the number of the monomeric unit, *n*, in a molecule. However, as the transfer of energy through chemical bonds may be restricted within several bonds, *m*, the *G* values of decomposition will be independent of *n* which is larger than *m*. This expectation is realized by Figs. 5, 6, 7 and 8, with the exception of $G(CH_4)$ from paraffins. The "*m*" number is evaluated in each series of $-(-CHR-)-_n$ to be as follows:

R	H	HO	CH_3CO	CH_3COO
m	ca. 6	>4	>2	>3

When R is H, that is, for hydrocarbons, *m* is given as ca. 6, while is not very different from the $m=12$ stated by Alexander and Charlesby.[59] The same reasoning may be applicable to the other series, in which the *G* values from monomeric compounds

TABLE V. A COMPARISON OF $G(H_2)$ VALUES FROM MONOMERS AND POLYMERS

Ethylbenzene60)	$G(H_2)=0.18$
Polystyrene61,62)	$G(H_2)=0.03$—0.04
Ethanol63-72)	$G(H_2)=3.5$—5.53
Polyvinylalcohol62)	$G(H_2)=1.6$
Polyethylene73-75)	$G(H_2)=3.75$—6.0
Polymethylene58)	$G(H_2)=5.4$

should be several times larger than those from the corresponding polymers. $G(H_2)$ from polyethylene is nearly equal to that obtained from polymethylene, as was to be expected. Table V compares the $G(H_2)$ values from monomers and polymers.

The curve of $G(CH_4)$ vs. $1/n$ for paraffins shows a different tendency from the curves of the others. This result may be explained similarly as far as the energy transfer is concerned, but the terminal effect must also be introduced. Methane is assumed to come from the rupture of the terminal C–C bonds, and it results only from the excitation of the $m/2$ carbon atoms from the terminal carbon atoms of both ends. Since the carbon atoms in the hydrocarbon molecule are assumed to be excited with an equal probability, the probability of the excitation of carbon atoms within $m/2$ from the terminals is m/n. If the G value of methane formation from hydrocarbons containing i carbon atoms is denoted by $G_i(CH_4)$, $G_n(CH_4)$ is expressed by the equation, $G_n(CH_4)=(m/n)G_m(CH_4)$, in the $n \geqq m$, region, and it decreases with an increase of n in the $n \leqq m$ region as well as the G values of the other products.

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