The Radiolysis of Ethylene Glycol Diacetate

By Toshiro Isoya, Kozo Hirota and Motoyoshi Hatada

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There have been a number of reports on the radiolysis, in the liquid phase, of various monoacetates[1-7] which have an ester group in the molecule, but the radiolysis of diacetate or polyacetate, each of which has two or more groups in the molecule, has not yet been reported. The present paper, which will describe the radiolysis of ethylene glycol diacetate (EGDA), the lowest member of diacetate, which was attempted in order to investigate the effect on radiolysis of the number of ester groups in the molecule; the paper will, it is hoped, make possible a better understanding of the radiolysis of such polymers as polyacetates, because diacetate may, in a way, be ragarded as the lowest member of these polymers.

Experimental

Material. — Commercially-available EGDA was refluxed with acetic acid and then purified by distillation in vacuo. By gas chromatographic analysis, two small peaks were found in the sample, before and after the peak of EGDA; the impurities, which could not be identified, were ca. 0.8%.

Irradiations.—In each run, a liquid sample of 2 ml. of EGDA was by the conventional vacuum technique, degassed in a glass ampoule fitted with a break seal; the ampoule was sealed off and was then 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 1.2×10^{16} eV. sec^{-1} ml^{-1}, the correction in the electron density difference between the sample and the dosimeter solution being taken into account.

The Analysis of the Liquid Products.—The liquid products were identified by gas chromatographic and mass spectrometric analyses. The gas chromatograph used was a Shimadzu GCIB apparatus, its operating conditions for identification being as follows: adsorbent=polyethyleneglycol (PEG) 6000; column temperature=65°C and 130°C, and adsorbent=dioctyl phthalate, column temperature=110°C, column length=3.75 m., and flow rate of the carrier gas (nitrogen)=30 cc./min. The fractions separated by the gas chromatograph were collected by fraction collectors and subjected to mass spectrometry in order to identify them. To obtain the data for kinetics, the following operating conditions were adopted: column length=3.75 m., adsorbent=PEG 6000, the flow rate of the carrier gas (nitrogen) =30 cc./min., column temperatures=65°C (and 135°C for only methyl cellosolve acetate).

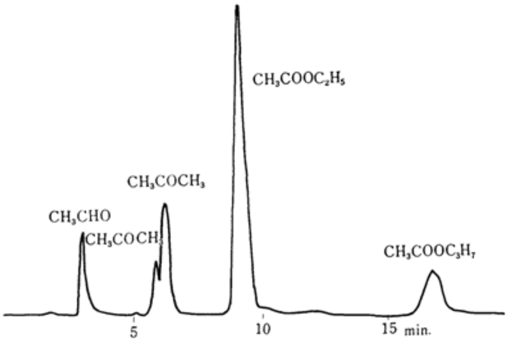

Fig. 1. Gas chromatogram of irradiated ethylene glycol diacetate.
PEG 6000 3.75 m.
N_2 gas 30 cc./min.
Column temp. 65°C

Figure 1 shows a typical gas chromatogram of the irradiated EGDA.

The Analysis of the Gaseous Products. — The gaseous products were separated into two fractions with a Toepler pump at −78°C and −196°C and were subjected to mass spectrometry.

The Measurement of the Mass Spectra.—The mass spectra were obtained by the use of a Hitachi RMU-5-type mass spectrometer, which was a 90°-sector-type instrument of magnetic scanning; the following conditions were adopted: accelerating potential=1500 V., bombarding electron voltage=90 V., and total electron current=100 μamp.

The Measurement of the ESR Spectrum.—The ESR spectrum was measured at −196°C on EGDA, which was degassed in a "Spectrosil" silica tube and irradiated with 1.5 MeV. electron beams (dose rate=9.3×10^{18} eV. g^{-1} sec^{-1}, and total dose=3.1×10^{21} eV. g^{-1}) from a Van de Graaff accelerator at −196°C. The apparatus was of the X-band type, equipped with a Varian V-4500 ESR spectrometer.

Results and Discussion

1) Figures 2 and 3 show the yields of products as a function of the energy absorbed.

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1) E. M. Kindermann, Report WADC-TR-57-465, Stanford Research Institute, September, 1957.

2) A. S. Newton and P. O. Strom, *J. Phys. Chem.*, **62**, 24 (1958).

3) G. E. Adams, J. H. Baxendale and R. D. Sedgwick, ibid., **63**, 854 (1959).

4) P. Ausloos and C. N. Trumbore, *J. Am. Chem. Soc.*, **81**, 3866 (1959).

5) R. W. Wagner and L. H. Towle, Report WADC-TR-58-683, Stanford Research Institute, March, 1959.

6) R. W. Hummel, *Trans. Faraday Soc.*, **56**, 234 (1960).

7) P. Ausloos, *J. Am. Chem. Soc.*, **83**, 1056 (1961).

The yields increased linearly with the dose in most cases; acetaldehyde and ethyl acetate were the exceptions. The *G* values of the eleven products are listed in Table I. These values were obtained from the best-fitting lines through the experimental points in Fig. 2 and Fig. 3.

TABLE I. *G* VALUES OF PRODUCTS
(dose rate 1.2×10^{16} eV. ml^{-1} sec^{-1})
(dose 6.3×10^{20} eV. ml^{-1})

Product	*G* Value
CH_4	0.70
C_2H_6	0.10
H_2	0.34
CO	0.76
CO_2	0.28
Acetaldehyde	1.4
Acetone	0.18
Methyl acetate	0.50
Ethyl acetate	1.0
n-Propyl acetate	0.25
Methyl cellosolve acetate	0.10

The effect of DPPH addition is shown in Table II. The yields of hydrogen, carbon dioxide, acetaldehyde and ethyl acetate decreased at the concentration of 5.5×10^{-3} mol./l., but the yields of the other products were scarcely affected at all by DPPH addition at this concentration. The yields of all the products, however, decreased as the concentration became higher. Some products were affected even at the lowest concentration (5.5×10^{-3} mol./l.), while other products were not, but all the products were affected at the highest concentration (9.2×10^{-2} mol./l.). DPPH may play not only the role of a scavenger of the radicals escaping from "cage," but also that of energy-acceptor.4)

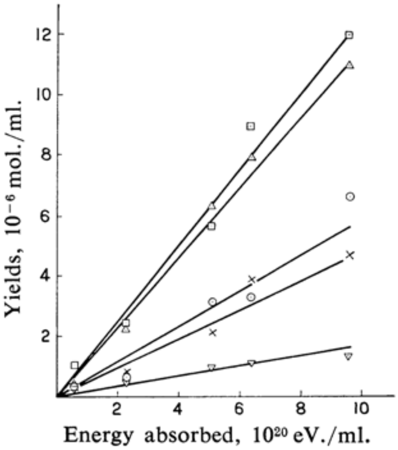

Fig. 2. Yields of gaseous products as a function of energy absorbed.
⊡ CO ⊙ H_2 ▽ C_2H_6
△ CH_4 × CO_2

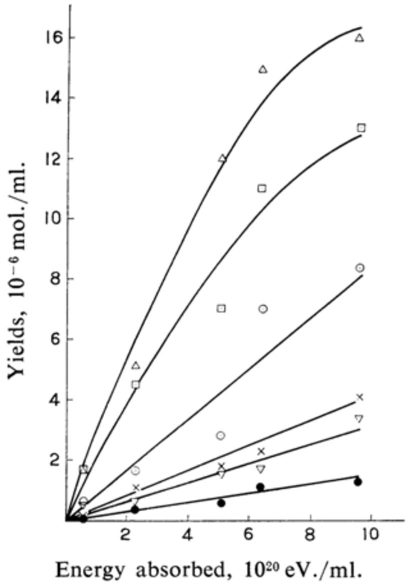

Fig. 3. Yields of liquid products as a function of energy absorbed.
△ CH_3CHO × $CH_3COOC_3H_7$
⊡ $CH_3COOC_2H_5$ ▽ CH_3COCH_3
⊙ CH_3COOCH_3 ● $CH_3OCH_2CH_2OOCCH_5$

Figure 4 shows the mass spectrum of EGDA. The ions of $m/e=29$ and 61 are assigned to HCO^+ and $CH_3COOH_2{}^+$, which are formed by some rearrangement processes. These rearrangement peaks have often been reported in the mass spectra of various acetates.[9-13] The ion of $m/e=86$ is assigned to $CH_3COOC_2H_3{}^+$, which may come from the C–O bond scission of the parent molecule after a rearrangement process including an H atom transfer, and the ion of $m/e=116$ may be formed by CH_2O elimination from the parent molecule.

Figure 5 shows the ESR spectrum of the irradiated EGDA.

This spectrum may be ascribed to CH_3COOCH_2 and/or $\dot{C}H_2COOCH_2CH_2OOCCH_3$.

The ratio of the number of carbon, hydrogen and oxygen atoms found in the products is calculated to be C : H : O = 5.0 : 10 : 2.7, clearly indicating that an excess of H is incorporated

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8) R. O. Bolt and J. G. Carroll, "Radiation Effects on Organic Materials," Academic Press, New York and London (1963).

9) A. G. Sharkey, Jr., J. L. Schultz and A. Friedel, *Anal. Chem.*, **31**, 87 (1959).

10) J. H. Beyonen, R. A. Saunders and A. E. Williams, ibid., **33**, 221 (1961).

11) E. W. Goldbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962).

12) C. E. Brion and W. J. Dunning, ibid., **59**, 647 (1963).

13) D. R. Black, W. H. McFadden and J. W. Corse, *J. Phys. Chem.*, **68**, 1237 (1964).

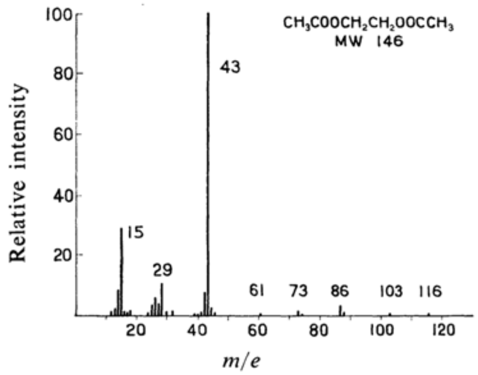


Fig. 4. Mass spectrum of ethylene glycol diacetate.

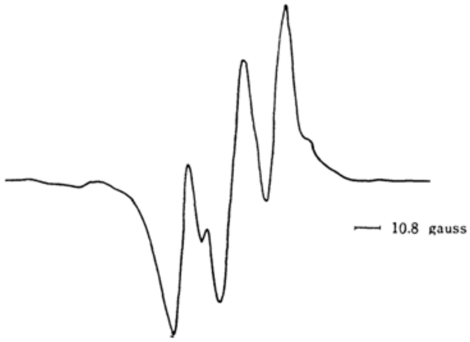


Fig. 5. ESR spectrum of irradiated ethylene glycol diacetate at −196°C.

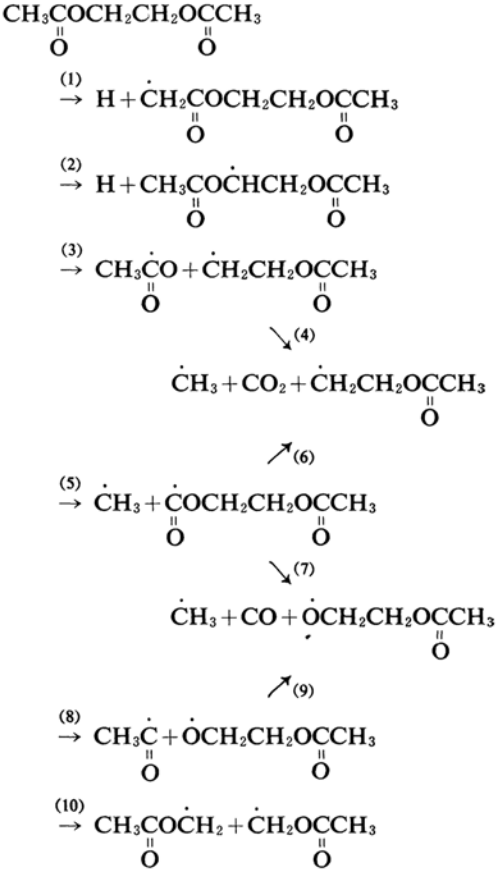
in the products in comparison with the empirical formula for EGDA, C : H : O = 6.0 : 10 : 4.0. In addition, a brown substance remained after the unreacted EGDA had been distilled away from the irradiated sample. The elemental analysis of this residue gave C : H : O = 6.2 : 10 : 4.1, the C and O contents being slightly larger than those of EGDA. These findings suggest the formation of such undetectable products as dimers, which may come from the radicals, $\dot{C}H_2COOCH_2CH_2OOCCH_3$ and $CH_3COO\dot{C}HCH_2OOCCH_3$, formed by the primary processes 1 and 2, as well as from unsaturated compounds of a higher molecular weight.

The dimers may be formed by the recombination reaction of radicals, $\dot{C}H_2COOCH_2CH_2OOCCH_3$ and/or $CH_3COO\dot{C}HCH_2OOCCH_3$. They may be produced by abstracting a hydrogen atom from EGDA with the radicals produced primarily, such as H, $\dot{C}H_3$, $CH_3\dot{C}O$, $CH_3COO\dot{C}H_2$ and $CH_3COOCH_2\dot{C}H_2$. On the above assumption, the yields of dimers may be given by the following equation:

$$G_{\mathrm{dimers}} = G_{H_2} + 1/2(G_{CH_4} + G_{CH_3CHO} + G_{CH_3COOCH_3} + G_{CH_3COOC_2H_5})$$

The G_{dimers} value calculated by this equation is 2.1, which gives a calculated C : H : O ratio of the system of 6.0 : 10 : 3.7, a ratio close to that of EGDA, 6.0 : 10 : 4.0.

2) The following reaction scheme is possible judging from the radiolytic products and the mass spectrum of EGDA. A part of the products can be explained by recombination reactions of these radicals.



$$\begin{aligned}
&CH_3\underset{\overset{\|}{O}}{C}OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\xrightarrow{(1)} H+\dot{C}H_2\underset{\overset{\|}{O}}{C}OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\xrightarrow{(2)} H+CH_3\underset{\overset{\|}{O}}{C}O\dot{C}HCH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\xrightarrow{(3)} CH_3\underset{\overset{\|}{O}}{\dot{C}}O+\dot{C}H_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\qquad\quad \searrow^{(4)}\\
&\qquad\qquad \dot{C}H_3+CO_2+\dot{C}H_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\qquad\quad \nearrow^{(6)}\\
&\xrightarrow{(5)} \dot{C}H_3+\underset{\overset{\|}{O}}{\dot{C}}OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\qquad\quad \searrow^{(7)}\\
&\qquad\qquad \dot{C}H_3+CO+\dot{O}CH_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\qquad\quad \nearrow^{(9)}\\
&\xrightarrow{(8)} CH_3\underset{\overset{\|}{O}}{\dot{C}}+\dot{O}CH_2CH_2O\underset{\overset{\|}{O}}{C}CH_3\\
&\xrightarrow{(10)} CH_3\underset{\overset{\|}{O}}{C}O\dot{C}H_2+\dot{C}H_2O\underset{\overset{\|}{O}}{C}CH_3
\end{aligned}$$

Some other products can be explained by the following rearrangement and recombination reactions:

$$CH_3COOCH_2CH_2OOCCH_3$$

$$\xrightarrow{(11)} CH_3COOCH_2CH_2OCH_3+CO$$

$$\xrightarrow{(12)} CH_3COOCH_2CH_2CH_3+CO_2$$

$$CH_3COOCH_2CH_2\dot{O}+\dot{C}H_3$$

$$\xrightarrow{(13)} CH_3COOCH_2CH_2OCH_3$$

$$CH_3COOCH_2\dot{C}H_2+\dot{C}H_3$$

$$\xrightarrow{(14)} CH_3COOCH_2CH_2CH_3$$

TABLE II. YIELDS IN THE PRESENCE OF DPPH
(dose rate 1.2×10^{16} eV. ml^{-1} sec^{-1})
(dose 6.3×10^{20} eV. ml^{-1})

$(10^{-6}$ mol./ml.)	Concentration of DPPH $(10^{-2}$ mol./l.)					Decrease* in the presence of DPPH
	9.2	6.5	1.3	0.55	0	%
H_2	1.7	1.5	1.8	1.9	3.3	48
CH_4	4.2	4.0	6.2	7.6	7.9	47
C_2H_6	0.9	0.9	1.0	1.2	1.1	18
CO	7.9	7.5	9.0	9.0	8.9	11
CO_2	2.4	2.4	2.4	2.8	3.9	38
Acetaldehyde	6.4	8.5	8.9	11.7	15.0	57
Acetone	1.2	1.3	2.0	2.6	2.7	56
Methyl acetate	1.4	1.4	1.4	2.1	2.0	80
Ethyl acetate	5.5	5.5	6.9	5.7	11.0	50
n-Propyl acetate	1.2	1.7	2.1	2.5	2.3	48
Methyl cellosolve acetate	0.90	0.75	1.0	1.1	1.1	18

* $(G_{\mathrm{DPPH(O)}}-G_{\mathrm{DPPH(9.2)}})/G_{\mathrm{DPPH(O)}}\times100$

Carbon monoxide is produced by the molecular rearrangement or the reaction in the cage 11, as well as by the radical decomposition processes 7 and 9. Similarly, carbon dioxide is produced by the reactions 12, 4 and 6. The effect of DPPH shows that a larger part of CO and CO_2 is produced through reactions 11 and 12, implying that a part of the methyl cellosolve acetate is formed by reaction 11, and the remaining part, by 13. Reactions 11 and 12 are supported by the ions of $m/e=28$ and $m/e=44$, ascribable to CO^+ and $CO_2{}^+$ respectively, in the mass spectrum of EGDA. *n*-Propyl acetate is formed by reactions 12 and 14. Reaction 12 proceeds almost as that reaction 14, judging from the effect of DPPH addition.

Ethyl acetate is formed by the reaction of such radicals as $CH_3COO\dot{C}H_2$ and $\dot{C}H_3$, $CH_3COOCH_2\dot{C}H_2$ and H, while hydrogen, methane, acetaldehyde, and methyl acetate are formed by the reaction of the hydrogen radical with the corresponding radical and by hydrogen abstraction by the three radicals from the parent molecule. Since the $CH_3CO\dot{O}$ radical is unstable,[14,15] the reaction of $CH_3CO\dot{O}$ and $\dot{C}H_3$ is disregarded; in fact, acetic acid was not actually found. 80% of the methyl acetate and 50% of the ethyl acetate were formed by some processes unaffected by DPPH.

Acetone and ethane are formed by the radical reactions 15 and 16 respectively, and to some extent by molecular processes in the cage:

$$CH_3\dot{C}O+\dot{C}H_3 \overset{(15)}{\rightarrow} CH_3COCH_3$$

$$\dot{C}H_3+\dot{C}H_3 \overset{(16)}{\rightarrow} C_2H_6$$

3) Most data on the monoacetates' radiolysis so far published have been obtained by electron-beam irradiation. In order to compare our results with those for monoacetates, the total gaseous yields of deaerated EGDA was determined by the use of electron irradiation from a Van de Graaff accelerator (dose rate: 1.0×10^{19} eV. ml^{-1} sec^{-1}, and dose: 6.7×10^{20} eV. ml^{-1} rads) at room temperature. The results are shown in Table III, as well as those for monoacetates.

TABLE III. TOTAL GASEOUS YIELDS OF VARIOUS ACETATES

	G_{gas}
Methyl acetate[1,8]	3.40
n-Propyl acetate[1,5,8]	2.4
Isopropyl acetate[1,5,8]	3.62
Benzyl acetate[1,5,8]	2.66
EGDA	1.45

The stability of EGDA against the radiation is about twice as much as that of the monoacetates. Similarly, as in the case of monoacetates, the most labile bond of EGDA is the acyl-oxygen bond, a finding from the product yields and from the mass spectrum of EGDA. The above conclusion implies that the yields of the products (acetaldehyde, acetone, carbon monoxide and methyl cellosolve acetate) formed by this bond scission are more than those of others formed by other bond scissions, the sum of the height of the peaks, $m/e=43$ (CH_3CO^+) and $m/e=103$ $(CH_3COOCH_2CH_2O^+)$, which result from this bond scission occupies

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14) L. Jaffe, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

15) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).

the largest part of the total ion intensity in the mass spectrum of EGDA.

In comparison with the yield of gaseous products from methyl acetate (MA) and EGDA (Table IV), the G_{MA}/G_{EGDA} ratio ranges between ca. 2 and 3. The molecular weights of MA and EGDA are 74.08 and 146.14, and the absorption energy per molecule of EGDA is about two times as much as that of MA. The ratio of the decomposition of MA to that of EGDA is 1.6, smaller than the others.

TABLE IV. G VALUES OF GASEOUS PRODUCTS OF METHYL ACETATE AND EGDA

	Methyl acetate	EGDA	G_{MA}/G_{EGDA}
G_{-M}	4.1 6)	2.5	1.6*
G_{H_2}	0.87(0.76) 4)	0.34	2.6(2.2)
G_{CO}	1.57(1.64)	0.76	2.1(2.2)
G_{CO_2}	0.78(0.95)	0.28	2.8(3.4)
G_{CH_4}	2.07(2.03)	0.70	3.0(2.9)
$G_{C_2H_6}$	0.27(0.34)	0.10	2.7(3.4)

* Only this numeral denotes the ratio of decomposition of MA to that of EGDA.

The yield of each gas per molecule of MA is 1—1.5 times as much as that of EGDA. This means that the formation mechanisms of these gaseous products from EGDA are very similar to those from MA.

Summary

The radiolysis of air-free ethylene glycol diacetate by ^{60}Co γ-rays has been studied at room temperature. The following results have been obtained: a) irradiation gives five gaseous products and six liquid products; b) the G value of the total of all the gaseous products is 2.18; c) the G value of the EGDA decomposition is 2.5. The effect of DPPH addition on the radiolytic products, the relation between radiolytic products and the mass spectrum of unirradiated EGDA, and the ESR spectrum of irradiated EGDA have also been studied. No remarkable difference in the products has been found between EGDA and various monoacetates except in the gaseous products, the yields from EGDA being 1/2—1/3 of those from methyl acetate.

Osaka Laboratories
Japanese Association for Radiation Research on Polymers
Neyagawa, Osaka (T. I., K. H. & M. H.)

Department of Chemistry
Faculty of Science
Osaka University
Toyonaka, Osaka (K. H.)

Technical Research Laboratory
Asahi Chemical Industry Co., Ltd.
Itabashi-ku, Tokyo (T. I.)