placement can be rationalized as being due to steric acceleration of ionization[9a] (exo hydrogens syn to the methyl group). The third point was for the *anti*-7-norbornenyl system for which our results given above indicate good agreement with the SBS correlation. However, we disagree both with respect to the Me/H ratio which was obtained by a rather elaborate extrapolation (see ref 17 on p 7803 of ref 12) and with the reported α-CH_3/CD_3 isotope effect. This effect was observed in the *p*-nitrobenzoates solvolyzed at 135° in 70% aqueous dioxane where complications due to acylcarbon oxygen cleavage may arise.

(30) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N.Y., 1969.

(31) (a) See ref 10, pp 177–182; (b) R. Eliason, S. Borčić, and D. E. Sunko, manuscript in preparation.

(32) The CH_3/H rate ratio for solvolysis of $RC{\equiv}CCCl(CH_3)_2$ is approximately 2000. This methyl effect would correspond in the SBS correlation to a CH_3/CD_3 rate effect of about 1.17; the observed value is 1.092.[33] Similarly, the CH_3/H rate ratio for solvolysis of $RC_6H_4CHClC_6H_5$ is approximately 30 and would correspond on the SBS correlation to a CH_3/CD_3 value of about 1.07; the observed values are solvent dependent and range from 1.025 to 1.058.[34] Thus these examples and one or two others[35] indicate that the CH_3/CD_3 isotope effects are proportionately smaller, relative to the CH_3/H rate effects at remote conjugated positions than they are at the α position. The reasons for this are not clear.

(33) V. J. Shiner, Jr., and G. S. Kriz, *J. Am. Chem. Soc.*, **86**, 2643 (1964).

(34) V. J. Shiner, Jr., and C. J. Verbanic, *J. Am. Chem. Soc.*, **79**, 373 (1957).

(35) See ref 10, p 153.

(36) P. J. Stang and T. E. Dueber, *J. Am. Chem. Soc.*, **95**, 2686 (1973).

(37) (a) S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957); (b) P. v. R. Schleyer and R. D. Nicholas, ibid., **83**, 182 (1961); (c) P. v. R. Schleyer, ibid., **86**, 1854 (1964).

(38) R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Am. Chem. Soc.*, **95**, 4860 (1973).

(39) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(40) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

(41) D. Kovačević, Ph.D. Thesis, University of Zagreb, 1972.

(42) The deuterium content of the alcohols was checked by NMR and was found to be greater than 2.94 atoms per molecule in the methyl group.

(43) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(44) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

(45) J. Jerkunica, Ph.D. Thesis, University of Zagreb, 1969.

Free-Radical Coupling, Cleavage, and Redox Reactions in ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives

Tibor Bernath, George H. Parsons, Jr., and Saul G. Cohen*

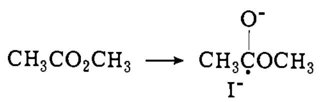
Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. *Received July 15, 1974*

Abstract: Reaction of methyl acetate with e^-_{aq} may lead to $CH_3C(O^-)OCH_3$ (I^-), $CH_3C(OH)OCH_3$ (II), and CH_3CO (IIA), and with ·OH and H· to $·CH_2CO_2CH_3$ (III), and to $CH_3CO_2CH_2·$ (IV). Methyl acetate is consumed, $G = -3.5$, and the loss is decreased by formate which scavenges ·H and ·OH, and increased by N_2O which converts e^-_{aq} to ·OH. Hydrogen is formed, $G = 1.1$, and this is decreased by scavengers for H·, and increased by H^+ which converts e^-_{aq} to H·. In radiolysis of 0.027 *M* methyl acetate, 1.5×10^{22} eV/l., radical combination products are: ethylene diacetate ($CH_3CO_2CH_2CH_2OCOCH_3$) (EDA), $G = 0.48$, from IV + IV; methyl β-acetoxypropionate ($CH_3CO_2CH_2CH_2CO_2CH_3$) (MAP), $G = 0.28$, from IV + III; dimethyl succinate (DMS), $G = 0.05$, from III + III; and a mixture of methyl acetoacetate and acetonyl acetate (MAA and AA), $G = 0.07$. Biacetyl is not observed. β-Mercaptopropionic acid, 0.0005 *M*, prevents formation of coupling products, as it reduces radicals III and IV, and thiyl radical oxidizes radical II back to methyl acetate. In a damaging cleavage, mercaptan reduces II and IIA to acetaldehyde, which is not formed in the absence of mercaptan. Biacetyl, H^+, N_2O, and H_2O_2 remove e^-_{aq} and I^-, II and IIA, and suppress MAA-AA; H^+ increases H·, III, and MAP, and DMS; N_2O and H_2O_2 increase ·OH, IV, and EDA. 2-Propanol, HCO_2^-, and CO scavenge ·OH and H· and suppress coupling products. Other sources of ·OH, Fenton's reagent and H_2O_2-uv, lead to EDA, MAP, and DMS with a high IV/III ratio. H· preferentially attacks acyl C–H; ·OH preferentially attacks alkoxyl C–H. Cleavage products (acetic acid, $G \sim 1.5$; methanol, $G \sim 1.0$) and small yields of methane and formaldehyde are found. Scavengers of e^-_{aq} or of H· and ·OH decrease acetic acid by half. Scavenging of all three fragments prevents formation of acetic acid, and hydrogen peroxide increases it. Radicals II and IIA may lead to ¾ of the acetic acid, IV to the remainder. Oxidation of them, largely by radical III, and in part by H_2O_2, is the suggested mechanism. Much of radical III is reduced back to methyl acetate. Cu^{2+}-Cu^{1+} strongly decrease coupling products and increase acetic acid, probably oxidizing IV and reducing III. Yields of radicals involved in formation of coupling products and acetic acid are estimated: G(II and IIA) = 1.2; G(III) = 1.4; G(IV) = 1.7. Part of the radicals, $G \sim 1.6$, regenerate methyl acetate by self-repair reduction of IV and III by II. Deuterium is introduced into methyl acetate during radiolysis in D_2O.

The effects of high-energy radiation on simple organic compounds in dilute aqueous solution are of interest, intrinsically and with respect to implications about corresponding reactions of high molecular weight materials and compounds of biological importance. In ^{60}Co γ irradiation of ~0.01 *M* aqueous solutions, >99.9% of the energy is absorbed by the water, leading to the reactive fragments,[1] the solvated electron, hydroxyl radical, and hydrogen atom, in molecules per 100 eV[2] [$G(e^-_{aq}) = 2.65$, $G(OH) = 2.72$, $G(H) = 0.55$], and to molecular products, hydrogen and hydrogen peroxide [$G(H_2) = 0.45$, $G(H_2O_2) = 0.68$]. The γ-ray-induced transformations of the solute result from their free radical-type reactions with the radiolytic products of the water.

Additives which scavenge or interconvert the reactive fragments modify the reactions and may indicate the nature of the reaction of the solute with each of the fragments. Formate ion removes H·, $k = 2.5 \times 10^9\ M^{-1}\ sec^{-1}$, and ·OH, $k = 2.2 \times 10^8\ M^{-1}\ sec^{-1}$, leading to $·CO_2^-$.[3] Nitrous oxide reacts with e^-_{aq}, leading to ·OH and N_2,[3,4] $k = 8.7 \times 10^9\ M^{-1}\ sec^{-1}$. Hydrogen peroxide reacts with e^-_{aq} and H·, leading to ·OH[3,5] with rate constants $1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$ and $5 \times 10^7\ M^{-1}\ sec^{-1}$, respectively, and with ·OH, leading to $HO_2·$,[3,6] $k = 4.5 \times 10^7\ M^{-1}\ sec^{-1}$. Mercaptan (RSH) reacts with the three fragments:[3,7] e^-_{aq} leads to HS^- and R·, $k = 5.0 \times 10^9\ M^{-1}\ sec^{-1}$; ·OH leads to RS·, $k = 3.0 \times 10^9\ M^{-1}\ sec^{-1}$; H· leads to R· and RS·, $k = 2.5 \times 10^9\ M^{-1}\ sec^{-1}$. Mercaptans and thiyl radicals also have high reactivity toward the radicals formed from organic solutes by reaction with the radiolytic fragments. These reactions may repair, by restoring the radicals to their original molecular states, or extend the damage by leading to further products.[9,10] In the γ radiolysis of aqueous solutions of alcohols,[10-15] H· and ·OH abstract H·, and the hydroxyalkyl radicals[16] lead to carbonyl compounds and glycols. In the radiolysis of 0.1 *M* 2-propanol, formation of acetone was diminished and pinacol fully suppressed by 0.003 *M* mercaptan,[10] as the 2-hydroxy-2-propyl radical was reduced to 2-propanol by mercaptan in a repair process, $k = 4.2 \times 10^8$ M^{-1} sec^{-1}.[8] In the γ radiolysis of aqueous acetone, acetonyl radicals are formed by abstraction of H· by H· and ·OH, and they couple to 2,5-hexanedione.[11,17] Electron capture by acetone forms the ketyl radical anion,[3] $pK_a = 12.2$,[18] and this leads to the 2-hydroxy-2-propyl radical and then to 2-propanol, $G \sim 0.3$–0.6. Formation of hexanedione was completely suppressed, but formation of 2-propanol was greatly increased by 0.003 *M* mercaptan, to $G \sim 3$.[10] The hydrogen-transfer reaction which inhibits radiation damage of 2-propanol increases damage of acetone.

We now report on the ^{60}Co γ radiolysis of dilute aqueous methyl acetate. This compound contains groups corresponding to those of both an alcohol or ether and a ketone, with the additional property of their being combined in an ester. Reaction with e^-_{aq} may involve addition to the carbonyl group, forming radical anion I$^-$, eq 1, which may add a pro-



$$e_{aq}^- + CH_3CO_2CH_3 \longrightarrow \underset{\text{I}^-}{CH_3\overset{O^-}{\overset{|}{\dot{C}}}OCH_3} \qquad (1)$$

$$k_1 = 8 \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

ton rapidly, forming radical II, $CH_3\dot{C}(OH)OCH_3$. The rate constant forreaction with e^-_{aq} may be estimated from a linear free-energy plot based on reaction of e^-_{aq} with other esters.[19] The electron adduct to glycine methyl ester has been observed, $pK_a = 11.1$, and the rapid transfer of the electron to various acceptors has been studied.[20] Dissociative electron capture may lead to acetyl radical IIA (eq 2). Reac-

$$e_{aq}^- + CH_3CO_2CH_3 \longrightarrow \underset{\text{IIA}}{CH_3\dot{C}{=}O} + HOCH_3 + OH^- \qquad (2)$$

tions with ·OH and H· may involve abstraction of H· from the acyl and alkoxyl groups, leading to radicals III and IV (eq 3 and 4).[19]

$$\cdot OH + CH_3CO_2CH_3 \longrightarrow \underset{\text{III}}{\cdot CH_2CO_2CH_3} + \underset{\text{IV}}{CH_3CO_2CH_2\cdot} \qquad (3)$$

$$k_3 = 7 \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

$$H\cdot + CH_3CO_2CH_3 \longrightarrow \text{III} + \text{IV} \qquad (4)$$

$$k_4 = 6 \times 10^4\ M^{-1}\ \text{sec}^{-1}$$

The formation of five solute-derived species leads to a complex study in the chemistry of free radicals. Also, as bifunctional species, esters may be small molecule models for polymeric materials. Combination reactions of radicals derived from them correspond to cross-linking, and cleavage reactions correspond to degradation, of the high molecular weight analogs. ^{60}Co γ radiolyses of undiluted methyl acetate and isopropyl acetate have been described.[21-23] Studies in dilute solution minimize direct radiolysis and reactions of excited states.

Experimental Section

Materials. Water was triply distilled. D_2O was distilled from $KMnO_4$-NaOD and $K_2Cr_2O_7$-D_2SO_4. D_2O, NaOD, and D_2SO_4 were from Merck Sharpe and Dohme. Sodium chloride, cuprous chloride, hydrogen peroxide (30%), ferrous sulfate, and ethylenediaminetetraacetic acid were from Fisher Scientific Co. Nitrous oxide, carbon monoxide, and methane were from Matheson. Sodium formate (Fisher) was dried at 110°. Methyl acetate (Fisher Reagent Grade) was distilled on a spinning-band column either from molecular sieves (4A) or from $FeSO_4$ after washing with $CaCl_2$ and $FeSO_4$. Impurities were less than 10^{-6} to 10^{-7} *M* by GLC. Ethyl acetate (Fisher) and methyl propionate (Eastman) were distilled on a spinning-band column. Acetone, 2-propanol, methanol, and ethanol (Fisher), acetaldehyde (Eastman Reagent Grade), and acetic acid (Baker) were redistilled. Ethylene glycol (Fisher) was used as received. β-Mercaptoethanol (Aldrich) and β-mercaptopropionic acid and 1-pentanethiol (Eastman) were distilled under nitrogen. 2-Aminoethanethiol hydrochloride (Aldrich) was used as received. β-Mercaptopropionic acid and 2-aminoethanethiol hydrochloride were converted to the sodium salt and the free base, respectively, by titration of an aqueous solution with NaOH.

Dimethyl succinate (Eastman) was distilled, bp 65° (2.3 mm). Ethylene diacetate (Eastman) was distilled, bp 74° (3.5 mm). Methyl 3-acetoxypropionate was prepared from β-propiolactone. The lactone was treated with NaOH in methanol leading to methyl β-hydroxypropionate, bp 71° (10 mm) [lit.[24] 70° (10 mm)]; this was treated with acetic anhydride and 1 drop of H_2SO_4, leading to the product, bp 71° (8 mm) [lit.[24] 81° (10 mm)]. The NMR spectrum, integrated, showed triplet at δ 3.91 (O-CH_2), a singlet at δ 3.32 (CH_3-O), a triplet at δ 2.30 (CH_2-CO), and a singlet at δ 1.68 (CH_3-CO). Acetonyl acetate (Chemical Procurement Laboratories) was used as received. Methyl acetoacetate (Eastman) was redistilled. Diethyl succinate (Eastman) was free of impurities on GLC on Carbowax 20M. 2,3-Dimethylsuccinic acid (Chemical Procurement Laboratories) was converted to the dimethyl ester, bp 78° (3.8 mm) [lit.[25] 198–199° (760 mm)]. Dimethyl 2-methylglutarate, bp 77° (22 mm), was prepared from the corresponding acid. Dimethyl adipate (Eastman) was redistilled. 2,3-Butanediol (Chemical Procurement Laboratories) and 1,3- and 1,4-butanediols (Eastman) were used as received. The butane diacetates were prepared by treatment of the diols with acetic anhydride and sulfuric acid: 2,3-butane diacetate, bp 164–166° (5 mm), 1,4-butane diacetate, bp 177° (5 mm), 1,3-butane diacetate, bp 175–176° (5 mm).

Irradiation. Solutions of the ester or the ester and additives were prepared in triply distilled water. Solutions were transferred to Pyrex irradiation cells, ~20 cm^3 capacity, fitted with fritted-glass discs. The cells were swept with argon for at least 15 min, capped with ground-glass stoppers, and irradiated for stated times. In control experiments, degassing by freeze–thaw cycles led to the same results as did argon sweeping. The argon was first passed through a solution of ester in water to minimize loss of ester in the sweeping. Irradiation was carried out with ^{60}Co γ-rays in a Model 220 Gammacell (Atomic Energy of Canada) with an initial flux of 3.3×10^{22} eV/l./hr. Doses were measured by Fricke dosimetry.[26]

Oxidation by Fenton's reagent was carried out with aqueous solutions of 0.027 *M* methyl acetate, 0.003 *M* hydrogen peroxide, and 0.003 *M* ferrous sulfate containing 1 ml of sulfuric acid per 100 ml. When complexed Fe^{2+} was used, a solution of 0.003 *M* 1:1 ethylenediaminetetraacetic acid-$FeSO_4$ and 0.027 *M* methyl acetate in 0.5 *M* buffer of Na_2HPO_4-KH_2PO_4, pH 7, was allowed to react. Oxidations were allowed to proceed for 10 minutes and were quenched with hydroxide. Ultraviolet-induced oxidations by hydrogen peroxide were carried out on aqueous solutions of 1% H_2O_2, 10% methyl acetate in a Rayonet apparatus, in quartz with 2537 Å irradiation to an extent of 20–30% decomposition of H_2O_2.

Analyses. Analyses for hydrogen were carried out as described previously.[10] Analysis for mercaptan was made with 1% $FeCl_3$, 0.25% *o*-phenanthroline, from the absorbance at 515 mμ.[27] Analysis for H_2O_2 was made by the potassium iodide procedure.[28] Consumption of methyl acetate was followed by injection of irradiated solutions on to a Perkin-Elmer Model 990 GLC instrument, with flame-ionization detector, 9 ft × ⅛ in. 15% Ucon Polar column, 65–75°, with ethyl acetate as an internal standard. Acetic acid was determined in the irradiated solutions (i) titrimetrically (to pH 7) with an Autoburette ABU 12 delivering 0025 *N* NaOH or (ii) by GLC on 6-ft columns, freshly packed with Porapaq Q, Porapaq Q-S, or Chromsorb 101, with ethanol as internal standard. The two methods agreed within 5–10%.[29] Methanol and acetaldehyde were determined in the irradiated solutions by GLC on a 6-ft Porapaq Q column at 80°. Analysis for formaldehyde was by a *p*-phenylenediamine-H_2O_2 colorimetric method.[30]

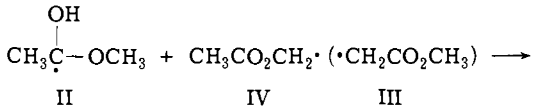
Analyses for radical coupling products, ethylene diacetate (EDA), methyl β-acetoxypropionate (MAP), dimethyl succinate (DMS), acetonyl acetate (AA), and methyl acetoacetate (MAA), were made by GLC and mass spectrometry. Diethyl succinate was added to the irradiated solution as an internal standard. The products were extracted from the irradiated solutions with three 10-ml portions of chloroform, and the extracts were dried and concentrated. Analysis was on a 9-ft 15% Carbowax 20M column at 150°. Synthetic mixtures of known composition were analyzed similarly. The appearance order was AA-MAA, EDA, MAP, DMS, and DES. Structures of the products were confirmed by comparison of retention times with those of authentic samples on UCON polar and Carbowax 20M columns and by comparison of fragmentation patterns with those of authentic samples[31] on a combined gas chromatograph-mass spectrometer. Use of a Perkin-Elmer RMU-6M mass spectrometer, equipped with appropriate GC columns was kindly made available by Dr. J. Wishnok, Boston University. Operation at 30 and 70 eV led to the same cracking patterns. Analyses for products from ethyl acetate and methyl propionate were made on 20% Carbowax 20M against authentic samples.

In the study of deuterium incorporation, methyl acetate was irradiated in D_2O, as described above for irradiations in H_2O. Distillation of the irradiated solution furnished an azeotrope, 95% methyl acetate-5% D_2O. This was examined by linked gas chromatography-mass spectrometry at an ionizing voltage of 30 eV.

Results and Discussion

G values for disappearance of methyl acetate were examined. Some results are summarized in Table I.

The *G* value for disappearance of methyl acetate, ~3.5, is higher than the yield of any one water fragment and less than the sum of the three, e^-_{aq}, ·H, and ·OH, 5.9. Radical II may disproportionate to some extent with radicals III and IV, regenerating methyl acetate in a repair process, eq 5, leading to less than maximum *G* values for radiolytic loss



$$\underset{\text{II}}{CH_3\overset{OH}{\dot{C}}-OCH_3} + \underset{\text{IV}}{CH_3CO_2CH_2\cdot}\ (\underset{\text{III}}{\cdot CH_2CO_2CH_3}) \longrightarrow 2CH_3CO_2CH_3 \quad (5)$$

of methyl acetate. When methyl acetate was subjected to γ radiation in D_2O, substantial D was found in the recovered methyl acetate, consistent with such self repair. This repair mechanism was also proposed in irradiation of acetamide.[9] Nitrous oxide and hydrogen peroxide led to additional ·OH, from e^-_{aq} and from e^-_{aq} and ·OH, respectively. This increased the destruction of ester to $G = -5.1$, indicating that ·OH alone is very effective in abstracting H· and damaging the ester (eq 3). Sodium formate scavenged H· and part of ·OH, decreasing their attack on the ester and its disappearance. It is possible that, in this system, $CO_2^-\cdot$, formed by abstraction of H· from formate, also repairs II, regenerating formate (eq 6).

$$\underset{\text{II}}{CH_3\dot{C}(OH)OCH_3} + CO_2^{-}\cdot \longrightarrow CH_3CO_2CH_3 + HCO_2^- \quad (6)$$

G values for formation of H_2, extrapolated to zero dose are summarized in Table II.

The yield of hydrogen, $G = 1.1$, was little more than the sum of the molecular yield from radiolysis of water and the yield of radiolytic H·, indicating that additional H_2 arises from abstraction of H· from the ester by H·. 2-Propanol scavenged H· and ·OH, converted H· to H_2, and left the yield of H_2 unchanged. Hydrogen peroxide scavenged e^-_{aq} and H· without forming H_2 and decreased H_2 to the molecular yield. The mercaptan scavenged about half the e^-_{aq} and ·OH, and all the H·, and also lowered the yield of H_2 to the molecular yield. Hydrogenolysis of the R-S bond and formation of H_2S may occur.[32] Acid, pH 2.6, converted e^-_{aq} in part to H· and doubled the yield of H_2. Sodium formate decreased H_2, possibly because of the increase in pH to which it led. As will be shown below, the solutions generally became acidic. The effects of the additives on yields of H_2 are consistent with their ability to scavenge H·, with or without formation of H_2, and to facilitate or prevent conversion of e^-_{aq} to H·.

Table I. ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives on Disappearance of Methyl Acetate

Dose × 10^{-22}, eV/l.	Additive		$CH_3CO_2CH_3$, *M*		
	Compd	*M*	Initial	Final	*G*
3.3			0.0130	0.0110	−3.6
6.3			0.0141	0.0106	−3.3
2.2	HCO_2Na	0.001	0.0111	0.0103	−2.2
3.3	N_2O	0.023	0.0112	0.0084	−5.1
3.1	H_2O_2	0.0041	0.0114	0.0087	−5.2
3.1			0.00351	0.00257	−1.8
3.1	N_2O	0.023	0.0048	0.0028	−3.9

Table II. ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives on Yields of H_2

$CH_3CO_2CH_3$, *M*	Additive		$G(H_2)$
	Compd	*M*	
0.010			1.1
0.056			1.1
0.010	$CH_3CHOHCH_3$	0.01	1.1
0.056	$HSCH_2CH_2CO_2H$	0.0004	0.4
0.010	H_2O_2	0.004	0.4
0.010	HCO_2Na	0.001	0.7
0.010	H_2SO_4, pH 2.6		2.1

Radical species I^-, II, IIA, III, and IV, formed according to eq 1-4, may lead to products of combination (eq 7-12).

$$\underset{\text{IV}}{2CH_3CO_2CH_2\cdot} \longrightarrow \underset{\text{ethylene diacetate (EDA)}}{CH_3CO_2CH_2CH_2OCOCH_3} \quad (7)$$

$$\underset{\text{III}}{2\cdot CH_2CO_2CH_3} \longrightarrow \underset{\text{dimethyl succinate (DMS)}}{CH_3O_2CCH_2CH_2CO_2CH_3} \quad (8)$$

$$\text{IV} + \text{III} \longrightarrow \underset{\text{methyl }\beta\text{-acetoxypropionate (MAP)}}{CH_3CO_2CH_2CH_2CO_2CH_3} \quad (9)$$

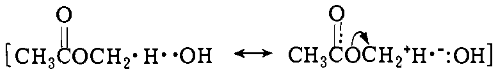
$$\underset{\text{II}}{CH_3\dot{C}(OH)OCH_3} + \text{IV} \longrightarrow \underset{\text{acetonyl acetate (AA)}}{CH_3COCH_2OCOCH_3} + CH_3OH \quad (10)$$

$$\text{II} + \text{III} \longrightarrow \underset{\text{methyl acetoacetate (MAA)}}{CH_3COCH_2CO_2CH_3} + CH_3OH \quad (11)$$

$$\text{II} + \text{II} \longrightarrow \underset{\text{biacetyl}}{CH_3COCOCH_3} + 2CH_3OH \quad (12)$$

Radical IIA ($CH_3\dot{C}{=}O$) may lead to the same products as II. Three products, EDA, MAP, and DMS were separated and analyzed by GLC; MAA and AA appeared as a mixture in low yield, and biacetyl was not observed. Some results are summarized in Table III.

The major product is EDA from dimerization of IV; somewhat less MAP, from cross-coupling of IV + III, is found, and DMS from two radicals III, and MAA and AA from II + III and II + IV are minor products. In irradiation of 0.5 *M* ester, *G* values of radicals IV, III, and II accounted for in these products are 1.5, 0.45, and ~0.08, respectively. The major hydrogen-abstracting species is ·OH, $G = 2.7$ compared with $G = 0.55$ for ·H. The electrophilic properties of ·OH[33] would favor abstraction from the alkoxyl group,[34] formula V, and this may account for the prepon-



V

$$[CH_3\overset{O}{\overset{\|}{C}}OCH_2\cdot H\cdot\cdot OH \longleftrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_2{}^{+}H\cdot{}^{-}{:}OH]$$

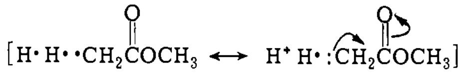
Cohen et al. / ^{60}Co γ Radiolysis of Aqueous Methyl Acetate

Table III. ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives on Formation of Coupling Products[a]

Dose × 10^{-22}, eV/l.	$CH_3CO_2CH_3$, *M*	Additive		Coupling products, *G*					Radical ratio, IV/II
		Compd	*M*	MAA–AA	EDA	MAP	DMS	Total	
0.48, 1.9	0.50			0.08	0.61	0.25	0.08	1.02	3.4
1.0	0.48	$HSCH_2CH_2CO_2H$	0.0005	0	0.06	0.02	0.005	0.09	5
1.5, 2.2	0.027			0.07	0.48	0.28	0.05	0.88	3.1
1.0	0.027	$HSCH_2CH_2CO_2H$	0.0005	0	0	0	0	0	
1.9	0.027	$HSCH_2CH_2CO_2H$	0.0005	0	0.05	0.03	0	0.08	4
2.9	0.027	$HSCH_2CH_2CO_2H$	0.0018	0	0	0	0	0	
1.5	0.027	$CH_3COCOCH_3$	0.0002	0.001	0.75	0.26		1.01	4
0.8	0.027	H_2SO_4	(pH 2.2)		0.38	0.56	0.18	1.12	1.4
1.6	0.027	H_2SO_4	(pH 2.2)	0.01	0.38	0.51	0.14	1.04	1.6
0.9	0.060	N_2O	0.023	0	1.0	0.66	0.04	1.7	3.6
1.9	0.060	N_2O	0.023	0	0.97	0.37	0.04	1.38	5.1
1.0	0.041	CH_3COCH_3	0.004	(0.24)	0.36	0.16	0.015		
2.2	0.027	$ClCH_2CO_2CH_3$	0.027		0.06	0.35	(0.6)		
2.9	0.027	NaCl	0.029	0.05	0.30	0.14	0.02	0.51	4.4
1.0, 2.2	0.027	$Cu^{1+,2+}$	0.0001	0	0.19	0	0	0.19	
1.0, 1.9	0.027	HCO_2^-	0.003	———	———	Traces	———		
1.0,[b] 2.9	0.010				0.46	0.33			
0.8,[b] 1.7	0.011	H_2O_2	0.004		0.54	0.21			
1.0[b]	0.010	CO	0.008					~0	
1.0,[b] 1.9	0.010	$CH_3CH(OH)CH_3$	0.010					~0	

[a] Methyl acetoacetate (MAA); acetonyl acetate (AA); ethylene diacetate (EDA); methyl acetoxypropionate (MAP); dimethyl succinate (DMS). [b] Early experiments in which analyses carried out directly on irradiated solutions; minor products, MAA–AA and DMS, were not observed.

derance of IV in the coupling products. The nucleophilic character of H· might favor abstraction of acyl C–H, formula VI.



$$[H\cdot H\cdot\cdot CH_2\overset{O}{\overset{\|}{C}}OCH_3 \longleftrightarrow H^+ H\cdot :CH_2\overset{O}{\overset{\|}{C}}OCH_3]$$

VI

That ·OH abstracts preferentially but not solely from the alkoxyl group is also seen in the results of oxidation of methyl acetate with Fenton's reagent and with uv-sensitized hydrogen peroxide, in which ·OH may be the sole oxidizing species. EDA predominated in the coupling products, and ratios of IV/III of about 5 were found. This ratio was increased further when Fenton's reagent was used in the presence of air, indicating that radical III may combine with O_2 more rapidly than does radical IV, presumably forming a hydroperoxy radical. An extreme was reached with Fenton's reagent in the presence of a complexing agent, EDTA. Only EDA was observed, the product from radical IV. Radical III was apparently reduced[35] under these conditions to methyl acetate.

Biacetyl, low pH, and N_2O scavenge e^-_{aq} and thus prevent formation of II and IIA and of MAA-AA. However, they lead to overall increase in coupling products. Acid, pH 2.2, converts e^-_{aq} to H· and increases MAP and DMS. The increase in coupling products corresponds to a twofold increase in content of radical III, indicating that H· abstracts H· largely from the acyl carbon, formula VI. Nitrous oxide converts e^-_{aq} to ·OH and greatly increases EDA. The increase in coupling product corresponds to a nearly twofold increase in content of radical IV. Similarly, H_2O_2 converts e^-_{aq} and H· to ·OH, and this increased EDA and decreased MAP. Ratios of IV/III in the coupling products were 1.5 at pH 2.2, because of increased H·, 3.1 in the absence of additive, 5.1 in the presence of N_2O, and ~6 in the presence of H_2O_2, as ·OH increased. These results are consistent and diagnostic as to the actions of H· and ·OH, but the coupling products do not reveal the true ratio of initially formed radicals since reactions other than coupling occur, and the coupling products themselves are consumed somewhat during irradiation.

Acetone competes favorably with ester for e^-_{aq} and H· but not for ·OH. The normal coupling products, EDA, MAP, and DMS, decreased, as acetonyl and 2-hydroxy-2-propyl radical from acetone appear to react with III and IV and lead to products in the MAA-AA peak. 2-Propanol and hexanedione were not observed. Methyl 2-chloroacetate scavenges e^-_{aq} by dissociation of Cl^-, but it itself leads to radical III, which appears as a high yield of DMS. Added Cl^- itself decreased coupling products, probably by reacting with ·OH, leading to ^-OH and the less reactive Cl·.

Cuprous–cupric ions, 10^{-4} *M*, led to a marked decrease in coupling products, and only the major one, EDA, was observed. This result may be due to repeated redox reactions. Cupric ion competes favorably with ester for e^-_{aq} and H·[3a,b] and is reduced thereby to Cu^{1+}, and Cu^{1+} may be reoxidized to Cu^{2+} by ·OH and H_2O_2. Radicals III and IV, formed to a lesser extent because of this scavenging of the radiolytic fragments, may also be reduced by Cu^{1+} and oxidized by Cu^{2+}, respectively, leading to further decreased coupling products.

Formate ion and 2-propanol, scavengers for ·H and ·OH but not for e^-_{aq}, and CO, scavenger for ·OH and e^-_{aq} and probably for H·, reduce coupling products essentially to zero. Pinacol was formed from 2-propanol, $G = 0.4$, and acetone appeared to be formed with $G = 1.85$ as compared with 0.8 in irradiation of aqueous 2-propanol in the absence of methyl acetate.[10] This may indicate that 2-hydroxy-2-propyl may transfer H to methyl acetate.

$$CH_3\dot{C}(OH)CH_3 + CH_3CO_2CH_3 \longrightarrow CH_3COCH_3 + \underset{\text{II}}{CH_3\dot{C}(OH)OCH_3}$$

Removal of H· and ·OH, preventing formation of III and IV, suffices to prevent formation of coupling products. Species I^-, II, and IIA, from e^-_{aq}, appear to lead to coupling products only in combination with III and IV and then in low yield. Radical II may be reoxidized to starting ester by IV and III (eq 5) or by H_2O_2, as are α-hydroxyalkyl radicals.[36] It will be seen that reactions of e^-_{aq} are important in leading to cleavage products, which are formed in high yields.

The effects of mercaptan merit separate attention since

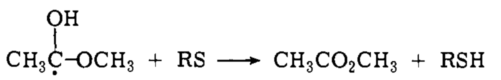
Table IV. ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives on Formation of Acetic Acid, Methanol, Acetaldehyde, and Hydrogen Peroxide

Dose × 10^{-22}, eV/l.	$CH_3CO_2CH_3$, *M*	Additive		CH_3CO_2H, *G*	CH_3OH, *G*	CH_3CHO, *G*	H_2O_2, *G*
		Compd	*M*				
0.83	0.50			4.7		0	
0.83	0.50	$HSCH_2CH_2CO_2H$	0.0006	1.7	~3	~3	0.01
1.66	0.50	$HSCH_2CH_2CO_2H$	0.0009	1.3	~3	~3	
0.83	0.060			1.9	1.2	0	0.21
1.66	0.060			1.4	0.7	0	0.15
0.83	0.060	$HSCH_2CH_2CO_2H$	0.0007	0.9	1.5	3.5	
1.66	0.060	$HSCH_2CH_2CO_2H$	0.0007	0.9	1.0	1.6	
0.83	0.060	N_2O	0.023	0.9	0.8	0	0.75
1.66	0.060	N_2O	0.023	1.0	0.5		0.60
0.83	0.061	N_2O $CH_3CHOHCH_3$	0.023 0.061	0			
0.83	0.01	$CH_3CHOHCH_3$	0.01	0.7			
0.41	0.060	N_2O $HSCH_2CH_2OH$	0.023 0.0006	<0.1	~0	~0	
1.66	0.040	CH_3COCH_3	0.004	0.3			0.06
1.53	0.060	$CH_3COCOCH_3$	0.0002	1.0			
0.83	0.028			1.5	1.0	0	0.17
1.66	0.028			1.4	0.5	0	
0.41	0.027	H_2O_2	0.010	2.6			
0.83	0.027	HCO_2Na	0.003	1.1	0.9	0	
1.66	0.027	HCO_2Na	0.003	1.0	0.6		
0.83	0.027	$Cu^{1+}Cu^{2+}$	0.0001	4.5		0	
1.66	0.027	$Cu^{1+}Cu^{2+}$	0.0001	3			
0.83	0.027	NaCl	0.029	2.2	0.7	0	
1.66	0.027	NaCl	0.029	2.5	0.4		

they may be due to reactions of the sulfur compounds with the several ester-derived radical species rather than with the radiolytic fragments from water. At 0.5 *M* ester and 0.0005 *M* mercaptan, the rate constants are such that 90% of the major fragments, e^-_{aq} and ·OH, react with the ester, while H· reacts largely with mercaptan. Yields of coupling product decreased by an order of magnitude; the small amount which was formed showed a high IV/III ratio, 5, consistent with scavenging of H·. The radicals which normally produce the major coupling products, IV and III, were formed by reaction of ·OH, but mercaptan reduced them and prevented their conversion to coupling products. This regenerated methyl acetate in a repair reaction (eq 13) which may

$$\underset{\text{IV}}{CH_3CO_2CH_2\cdot}\ (\underset{\text{III}}{\cdot CH_2CO_2CH_3}) + RSH \longrightarrow CH_3CO_2CH_3 + RS\cdot \qquad (13)$$

compete favorably with radical combination.[10] The thiyl radical may be reduced to mercaptan by radical II (eq 14),



$$\underset{\text{II}}{CH_3\overset{OH}{\overset{|}{\dot{C}}}{-}OCH_3} + RS \longrightarrow CH_3CO_2CH_3 + RSH \qquad (14)$$

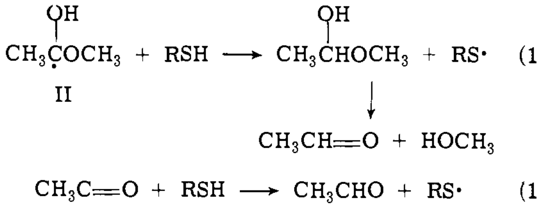
and the sulfur compounds may be used repeatedly in their two oxidation states,[37] regenerating methyl acetate in both processes. Evidence for occurrence of the reaction of eq 13 is indicated in a radiolysis in D_2O of 0.027 *M* methyl acetate and 0.0005 *M* mercaptan, in which the ester was protected (Table III), and increased incorporation of D was observed, $G \sim 3$, after 1×10^{22} eV/l. Lower initial concentrations of ester help measurement of the introduction of D but, at lower ester to mercaptan ratios, more scavenging by mercaptan of the radiolytic fragments from water also occurs.

^{60}Co γ irradiation of aqueous methyl acetate led also to products of cleavage of the ester. Acetic acid formed quickly, and pH values of 4.1–4.5 were observed after 0.83×10^{22} eV/l. irradiation. Presence of N_2O led to less acid, pH >5, and sodium formate and acetone led to still less acid, pH ~6. Copper salts, 10^{-4} *M*, led to increased acidity, pH <4. Results of analyses for cleavage products are summarized in Table IV.

Cleavage of methyl acetate, and formation of acetic acid, is a major process in this radiolysis. Yields of acetic acid are higher at higher initial concentrations of ester and at lower irradiation times. The yield of acetic acid, $G \sim 1.5$, plus the ester moieties in coupling products, $G \sim 1.8$, total 3.3, from irradiation of 0.027 *M* ester, may be compared with loss of methyl acetate (Table I), $G = -3.6$. The two kinds of experiments are done under different conditions, *G* (−methyl acetate) being determined at lower initial ester concentration and higher dose so that the loss can be measured. The discrepancy may be somewhat greater than indicated above and may be due, in part, to radiolytic loss of the products, which was observed in separate experiments.

Nitrous oxide scavenged e^-_{aq} and decreased acetic acid by one-half. Formate ion or 2-propanol, scavenging H· and ·OH, decreased acetic acid by about one-fourth. Acetone, scavenging e^-_{aq} and ·OH, decreased acetic acid drastically, while N_2O and 2-propanol combined, scavenging e^-_{aq}, ·OH, and H·, completely prevented formation of the acid. This indicates that hydrolysis of excited ester or hydrolysis by excited water is not important under these conditions. That N_2O doubles the amount of ·OH as it removes e^-_{aq}, and halves the yield of acetic acid thereby, indicates that normally about ¾ of the acid arises from a product of action of e^-_{aq} on the ester, the remainder from a product of action of ·OH.

Mercaptan strongly affects the cleavage reactions. It decreases acetic acid, leads to high yields of acetaldehyde, which compound was not detected in any experiments in the absence of mercaptan, and it increases the yield of methanol. Radicals II or IIA, which might otherwise lead to acetic acid, appear to be reduced by mercaptan (eq 15). Reac-



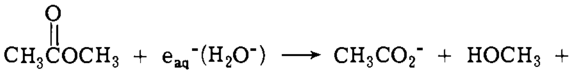
$$\underset{\text{II}}{CH_3\overset{OH}{\overset{|}{\dot{C}}}OCH_3} + RSH \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HOCH_3 + RS\cdot \qquad (15a)$$

$$CH_3\overset{OH}{\overset{|}{C}}HOCH_3 \longrightarrow CH_3CH{=}O + HOCH_3$$

$$\underset{\text{IIA}}{CH_3\dot{C}{=}O} + RSH \longrightarrow CH_3CHO + RS\cdot \qquad (15b)$$

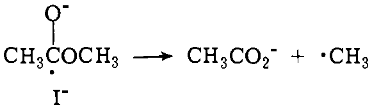
tions of eq 14 and 15a call for oxidation and reduction of the same radical by thiyl and mercaptan, respectively. This has been demonstrated for ketyl radicals.[37] In reducing radicals III or IV (eq 13), the mercaptan repairs ester and prevents coupling, and this would correspond to preventing radiation-induced cross-linking of a polyester. However, the similar hydrogen-transfer reaction, in reduction of II (eq 15a), damages and would correspond to chain rupture. That a one-electron reduction of an intermediate by mercaptan leads to acetaldehyde at the expense of acetic acid indicates that a one-electron oxidation of the intermediate is involved in forming acetic acid. Effects of H_2O_2, copper ion, and Cl^- (presumably as Cl·) in increasing acetic acid also indicate an oxidative rather than hydrolytic origin of the acid.

Reaction of e^-_{aq}, which appears to lead to ¾ of the acetic acid, may form $CH_3\dot{C}{=}O$ (IIA) and CH_3O^-, directly by eq 2 or by decomposition of $CH_3\dot{C}(O^-)OCH_3$ (I^-), and I^- may form $CH_3\dot{C}(OH)OCH_3$ (II). A cleavage of acetic acid analogous to that of eq 2 for the ester has been proposed.[38] Reaction of e^-_{aq} to form $CH_3C^-{=}O$ and $CH_3O\cdot$ does not occur since acetaldehyde is not observed in the absence of mercaptan. The solvated electron, formulated instead as H_2O^-, might act as a source of ^-OH and hydrolyze the ester (eq 16). This would comprise an ester mediated conversion of e^-_{aq} to H·. There is no evidence for this in the yield of H_2, and the effect of added H^+ in leading to H· and its products indicates that ester alone does not effect this. The reaction of eq 16 appears unimportant under the slightly acidic conditions of these experiments.



$$CH_3\overset{O}{\overset{\|}{C}}OCH_3 + e_{aq}^-(H_2O^-) \longrightarrow CH_3CO_2^- + HOCH_3 + H\cdot \qquad (16)$$

Species I^- or II might dissociate into acetate ion (acetic acid) and methyl radical (eq 17). A little methane is observed, $G \sim 0.1$, but it might be formed by decomposition of acetyl radical IIA. Some methyl propionate is also detected, probably from coupling of $CH_3\cdot$ and radical III. Both methane and methyl propionate are decreased to $G \sim 0$ in the presence of mercaptan. Since mercaptan would reduce methyl to methane, that it prevents formation of methane instead of increasing it by competing with the coupling, indicates that it acts on a precursor, i.e., by reducing I^-, II, or IIA and leading to acetaldehyde (eq 15). In any event, the yield of methyl and its products is small, and reaction 17 is not an important source of acetic acid.

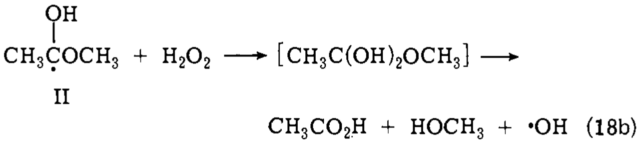


$$\underset{I^-}{CH_3\overset{O^-}{\overset{|}{\dot{C}}}OCH_3} \longrightarrow CH_3CO_2^- + \cdot CH_3 \qquad (17)$$

The fragment H· might cleave the ester to (a) $CH_3\dot{C}{=}O + HOCH_3$ or (b) to $CH_3CHO + \cdot OCH_3$. Course b is ruled out since acetaldehyde is not normally observed. Course a, or direct formation of radical II, is possible, but abstraction (eq 4) seems more rapid, and H· appears to lead to H_2. The fragment ·OH appears not to cause cleavage to $CH_3CO_2H + CH_3O\cdot$ since an increase in ·OH, resulting from presence of N_2O, leads to less cleavage and more coupling. The predominant reactions of ·OH also are abstractions (eq 3). Also, reactions of radiolytic fragments which might lead to $CH_3O\cdot$ would lead to an excess of products of radicals over the G values for the fragments, and this is not observed.

Acetic acid, it appears, is formed largely by oxidation of IIA, II, and I^- in processes, which overall lead to an equivalent amount of methanol, and by oxidation of IV which may lead to formaldehyde, some of which is detected. The rate constants and relative concentrations are such that ·OH reacts with ester (eq 3) and is not an important oxidizing agent for the radicals. Hydrogen peroxide, a relatively stable radiolytic product, is a possible oxidizer[36a] (eq 18). The

$$\underset{IIA}{CH_3\dot{C}{=}O} + H_2O_2 \longrightarrow CH_3CO_2H + HO\cdot \qquad (18a)$$

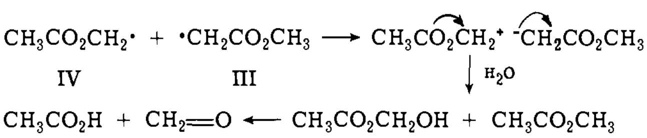


$$\underset{II}{CH_3\overset{OH}{\overset{|}{\dot{C}}}OCH_3} + H_2O_2 \longrightarrow [CH_3C(OH)_2OCH_3] \longrightarrow CH_3CO_2H + HOCH_3 + \cdot OH \qquad (18b)$$

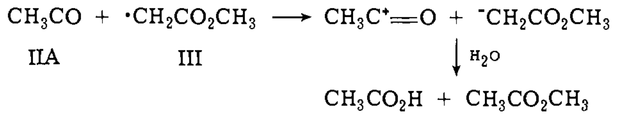
$$\underset{IV}{CH_3CO_2CH_2\cdot} + H_2O_2 \longrightarrow [CH_3CO_2CH_2OH] \longrightarrow CH_3CO_2H + CH_2{=}O + \cdot OH \qquad (18c)$$

increase in yield of acetic acid when H_2O_2 is added is presumably due to reactions of this type. However, the radiolytic yield of H_2O_2 is insufficient to account for the amount of acetic acid formed, and not all of it is consumed. That a higher concentration persists in the presence of N_2O indicates that species IIA and II may indeed be oxidized by H_2O_2, or that some of the radiolytic H_2O_2 may be reduced normally by e^-_{aq}.

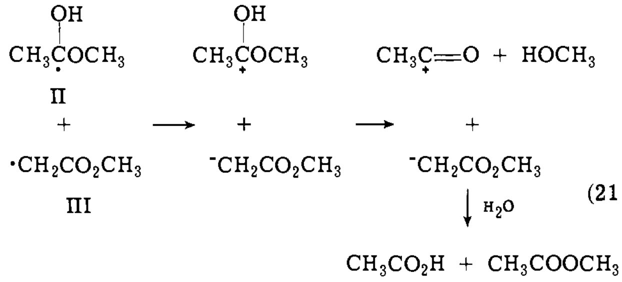
Radical III may be the important oxidizing agent. Combination of radicals IV and III leads to MAP (eq 9), but disproportionation is reasonable (eq 19) since IV has reducing properties, and III has oxidizing properties, as indicated in formulas V and VI. Radicals IIA and II also have reducing properties and, while their combination with III leads to the low observed yield of MAA (eq 11), disproportionation may be the major reactions. Oxidation of IIA by III is straightforward (eq 20), and methanol would have been formed in the prior step (eq 2). Oxidation of II by III (eq 21) would require that the intermediate cation, perhaps in an ion pair, loses methanol before it loses a proton and regenerates methyl acetate, in addition to the ester formed from III in these reactions. The balance between combination and disproportionation of like radicals in aqueous solution is a delicate one;[39] with potential redox pairs, disproportionation may be quite important in aqueous media. The major reaction of e^-_{aq} may be to lead to IIA (eq 2) and not to II (eq 1), and reaction 20 may lead to much of the acetic acid.



$$\underset{IV}{CH_3CO_2CH_2\cdot} + \underset{III}{\cdot CH_2CO_2CH_3} \longrightarrow CH_3CO_2CH_2^+\ {}^-CH_2CO_2CH_3 \xrightarrow{H_2O} CH_3CO_2CH_2OH + CH_3CO_2CH_3 \longrightarrow CH_3CO_2H + CH_2{=}O \qquad (19)$$



$$\underset{IIA}{CH_3CO} + \underset{III}{\cdot CH_2CO_2CH_3} \longrightarrow CH_3C^+{=}O + {}^-CH_2CO_2CH_3 \xrightarrow{H_2O} CH_3CO_2H + CH_3CO_2CH_3 \qquad (20)$$



$$\begin{array}{ccccc} \underset{II}{CH_3\overset{OH}{\overset{|}{\dot{C}}}OCH_3} & & CH_3\overset{OH}{\overset{|}{\underset{+}{C}}}OCH_3 & & CH_3\underset{+}{C}{=}O + HOCH_3 \\ + & \longrightarrow & + & \longrightarrow & + \\ \underset{III}{\cdot CH_2CO_2CH_3} & & {}^-CH_2CO_2CH_3 & & {}^-CH_2CO_2CH_3 \\ & & & & \downarrow H_2O \\ & & & & CH_3CO_2H + CH_3COOCH_3 \end{array} \qquad (21)$$

Particularly important effects of redox reactions on yields of both acetic acid and coupling products appear in the presence of cupric and cuprous ions.[33,40,41] Oxidation of radicals IIA and IV by Cu^{2+} may lead to acetic acid, reduction of radical III by Cu^{1+} may regenerate methyl acetate, the copper may be regenerated in its alternate valence states and used repeatedly, all coupling products are decreased, and acetic acid is increased.

Mercaptan alone diverts part of IIA from acetic acid to acetaldehyde. Mercaptan and N_2O together eliminate acetic acid completely. Mercaptan, reducing IIA, III, and IV, competes very effectively with disproportionation of III and IV, as it does with their combination, and less effectively with the rapid oxidation of IIA by III.

In the absence of additives, in irradiation of 0.028 M ester, G(acetic acid) = 1.5. If this arises from IIA (or II) and IV in ratio of 3:1, oxidized by H_2O_2, $G \sim 0.5$, and by III, $G \sim 1.0$, yields of IIA, III, and IV involved in this part of the reactions are $G(\mathrm{II}) = 1.1$, $G(\mathrm{III}) = 1.0$, $G(\mathrm{IV}) = 0.4$. Coupling products formed with $G = 0.88$, and their composition indicated $G(\mathrm{II}) = 0.1$, $G(\mathrm{III}) = 0.4$, and $G(\mathrm{IV}) = 1.3$. Total values accounted for are: $G(\mathrm{II,IIA}) = 1.2$, of which essentially all lead to acetic acid and other cleavage products; $G(\mathrm{III}) = 1.4$, of which $G = 1.0$ are oxidizing radicals reduced back to methyl acetate, and the remainder appear in coupling products; and $G(\mathrm{IV}) = 1.7$, of which $G = 0.4$ are oxidized to acetic acid, and the remainder appear in coupling products. All three radical species are implicated in products in substantial yield and not very unequally as would be indicated by consideration of coupling products alone. The total yield of radicals accounted for is $G = 4.3$, of which 2.5 lead to acetic acid and other cleavage products, 1.8 to coupling products. The total yield of reactive fragments from water is $G = 5.9$, and the difference, $G = 1.6$, may be a measure of the self-repair process (eq 5) in which radical II, $G \sim 0.8$, reduces an equivalent yield of the III + IV, regenerating methyl acetate.

Ethyl Acetate and Methyl Propionate. In preliminary studies, γ radiolysis of 0.02 M ethyl acetate, 3.3×10^{22} eV/l., led to 1,3-butane diacetate and 2,3-butane diacetate, from abstraction of H from the alkoxyl carbons. Methyl propionate led to dimethyl 2,3-dimethylsuccinate and dimethyl 2-methylglutarate, G for each ~ 0.2, and dimethyl adipate, $G < 0.1$, from abstraction of H· from acyl carbons, and mixed cross-coupling products containing the radicals from abstraction of alkoxyl H· and acyl derived radicals, $G \sim 0.3$.

Acknowledgment. This work was supported by the U.S. Atomic Energy Commission Grants AT(30-1)2499 and AT(11-1)3118.

References and Notes

(1) J. W. T. Spinks and R. J. Wood, "Introduction to Radiation Chemistry", Wiley, New York, N.Y., 1964, p 58.
(2) I. G. Draganic, M. T. Nendrovic, and Z. D. Dvaganic, *J. Phys. Chem.*, **73**, 2565 (1965).
(3) (a) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isot.*, **18**, 493 (1967); (b) M. Anbar, M. Banzbenek, and A. B. Ross, "Selected Specific Rates of Reactions of Transients from Water in Aqueous Solutions. 1. Hydrated Electron", U.S. Department of Commerce, NSRDS-NBS43, May 1973.
(4) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discuss. Faraday Soc.*, **36**, 193 (1963).
(5) E. J. Hart, *J. Am. Chem. Soc.*, **73**, 68 (1951).
(6) J. H. Baxendale in *Radiat. Res., Suppl.*, **No. 4**, 114 (1964).
(7) (a) A. Al-Thannon, R. M. Peterson, and C. N. Trumbore, *Trans. Faraday Soc.*, **64**, 2395 (1968); (b) M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, **77**, 990 (1973), and references cited therein.
(8) G. E. Adams, G. S. McNaughton, and B. D. Michael, *Trans. Faraday Soc.*, **64**, 902 (1968).
(9) J. Holian and W. M. Garrison, *Nature* (*London*), **221**, 57 (1969); *J. Phys. Chem.*, **72**, 758 (1968).
(10) S. G. Cohen and F. L. Lam, *Radiat. Res.*, **45**, 462 (1971).
(11) H. Fricke, E. J. Hart, and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).
(12) A. Glassner and E. J. Hart in *Radiat. Res., Suppl.*, **No. 4**, 74 (1964).
(13) (a) G. Jayson, G. Scholes, and J. J. Weiss, *J. Chem. Soc.*, 1358 (1957); J. T. Allan, E. Hayon, and J. J. Weiss., *ibid.*, 3913 (1959).
(14) J. T. Allan and G. Scholes, *Nature* (*London*), **187**, 218 (1960).
(15) T. Sawai, *Bull. Chem. Soc. Jpn.*, **39**, 955 (1966).
(16) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969).
(17) P. Reisz, *J. Phys. Chem.*, **69**, 1366 (1965).
(18) K. D. Asmus, A. Henglein, A. Wigger, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **72**, 529 (1968).
(19) E. J. Hart, E. M. Fielden, and M. Anbar, *J. Phys. Chem.*, **71**, 3993 (1967).
(20) M. Simic and E. Hayon, *Radiat. Res.*, **48**, 244 (1971).
(21) R. W. Hummel, *Trans. Faraday Soc.*, **56**, 234 (1960).
(22) A. S. Newton and P. O. Storm, *J. Phys. Chem.*, **62**, 24 (1958).
(23) P. B. Ayscough and J. P. Oversby, *J. Chem. Soc., Faraday Trans. 1*, 1153 (1972).
(24) M. L. Fein and C. H. Fisher, *J. Org. Chem.*, **13**, 749 (1948).
(25) M. Zelinski and P. Krapiwin, *Ber.*, **22**, 650 (1960).
(26) Reference 1, pp 106, 268.
(27) Procedure adapted from H. E. Zittel, *Anal. Chim. Acta*, **58**, 323 (1972).
(28) A. O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).
(29) R. G. Ackman, *J. Chromatogr. Sci.*, **10**, 560 (1972); R. B. H. Wills, *ibid.*, **10**, 582 (1972); G. I. Goodfellow and H. M. Webber, *Chem. Ind.* (*London*), 127 (1972).
(30) B. W. Bailey and J. M. Rankin, *Anal. Chem.*, **43**, 783 (1971).
(31) The mass spectrum of EDA was described: T. Isoya, K. Hirota, and M. Hatada, *Bull. Chem. Soc. Jpn.*, **38**, 1722 (1965). A general fragmentation of diesters and methyl esters is described in R. Ryhage and E. Stenhagen, *Ark. Kemi*, **14**, 497 (1959).
(32) M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, **77**, 990 (1973), and references cited therein.
(33) C. Walling, G. M. El-Taliawi, and R. A. Johnson, *J. Am. Chem. Soc.*, **96**, 133 (1974).
(34) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. B*, 742 (1966).
(35) C. Walling and G. M. El-Taliawi, *J. Am. Chem. Soc.*, **95**, 844 (1973).
(36) (a) C. E. Burchill and I. S. Ginns, *Can. J. Chem.*, **48**, 1232 (1970); (b) B. P. Roberts and K. E. Ingold in "Free Radical Substitution Reactions", Wiley-Interscience, New York, N.Y., 1971, p 192.
(37) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964).
(38) E. Hayon and J. Weiss, *J. Chem. Soc.*, 5091 (1960).
(39) S. G. Cohen, G. C. Ramsay, N. M. Stein, and S. Y. Weinstein, *J. Am. Chem. Soc.*, **96**, 5124 (1974).
(40) W. M. Garrison in "Current Topics in Radiation Research", Vol. IV, M. Ebert, Ed., North-Holland Publishing Co., Amsterdam, 1968, Chapter II.
(41) J. K. Kochi in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 11.