THE RADIOLYSIS OF DEUTERATED AND TRITIATED ACETIC ACIDS

BY JOHN G. BURR[1]

Contribution from the Chemistry Division of the Oak Ridge National Laboratory, Oak Ridge, Tenn.[2]

Received June 19, 1957

The deuterium content of the methane formed by radiolysis of deuterated acetic acids, and the tritium content of methane formed from tritiated acetic acids, both indicate that methane is formed from acetic acid almost exclusively by a radical process in which the intermediate methyl radicals abstract hydrogen almost entirely from the methyl group of acetic acid. The isotope content of the hydrogen produced in these irradiations, together with the rates of hydrogen production ($G(H_2)$ values) suggest, although less conclusively than for methane, a radical process as the origin for hydrogen. The origin of methane by a radical process in the irradiation of liquid acetic acid is compared with the evidence for a similar radical process in the fragmentation of CH_3COOH by electron impact in the highly dilute gas (mass spectrum).

Introduction

The present work is concerned with the mechanisms by which methane and hydrogen are formed in the γ-ray irradiation of pure liquid degassed acetic acid. A survey of the literature indicates that there is apparently no information about the effects of electron or γ-irradiation on pure liquid degassed acetic acid, nor about the non-volatile products formed in any irradiation of pure acetic acid. The effect of 27 Mev. α-particles upon acetic acid is to form CO_2 (4.0),[3] methane (1.38), ethane (0.85), hydrogen (0.52), and CO (0.4).[4] The data of Garrison,[4] *et al.*, suggest that non-volatile products are not formed in the helium ion irradiation of pure acetic acid. The action of α-particles from radon[5] on solid acetic acid at 0° produced hydrogen (0.8), methane (1.1), CO_2 (2.8) and CO (0.5).

Methane may be considered to be formed by either one or a mixture of two mechanisms: a molecular process (1), or a radical process (2)

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad (1)$$

$$CH_3COOH \longrightarrow CH_3 + COOH \quad (2)$$

$$CH_3 + CH_3COOH \longrightarrow CH_4 + CH_2COOH \text{ or } CH_3COO$$

Similarly, the formation of hydrogen may be considered to occur through either a molecular process (3) or a radical process (4)

$$2CH_3COOH \longrightarrow H_2 + \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} \quad (3)$$

$$CH_3COOH \longrightarrow H + CH_2COOH \text{ or } CH_3COO\cdot \quad (4)$$

$$H + CH_3COOH \longrightarrow H_2 + CH_2COOH \text{ or } CH_3COO\cdot$$

The radical processes present further problems worthy of examination: namely, whether the hydrogen abstraction reactions of the methyl radical and the hydrogen atom with substrate acetic acid molecules occur selectively or statistically. Solutions to these problems have been sought by studying the irradiation of acetic acid molecules which have been selectively labeled with deuterium or tritium. The substances which have been prepared and irradiated are CD_3COOH, CH_3COOD, $CH_3(t)COOH$, and CH_3COOH (t).

(1) Atomics International, P. O. Box 309, Canoga Park, California.

(2) Work done at the Oak Ridge National Laboratory.

(3) The numbers in parentheses are the G-values for yield in molecules per 100 e.v. of energy absorbed.

(4) A. S. Newton, AEC Report URCL-2455 (1954); similar data may be obtained by extrapolation from the work of Garrison, Bennett, Cole, Haymond and Weeks on aqueous acetic acid, *J. Am. Chem. Soc.*, **77**, 2720 (1955).

(5) W. L. Whitehead, C. Goodman and I. A. Breger, *J. Chem. Phys.*, **48**, 184 (1951).

Methods

1. Preparation of Labeled Molecules. CH_3COOD and $CH_3COOH(t)$.—These were each prepared by heating redistilled acetic anhydride with the calculated amount of D_2O in one case and tritiated H_2O (72.5 uc./mmole tritium content) in the other case. The cooled homogeneous solution was thoroughly dried over Drierite until both infrared spectra and/or Vapor Fractometer analysis showed the isotopic purity to be good and the water content negligible.

CD_3COOH.—A portion of completely deuterated acetic acid, prepared by threefold exchange of equal weights of malonic acid and D_2O and subsequent thermal decomposition of the perdeuteromalonic acid, was neutralized with 5 N sodium hydroxide. This solution was vacuum evaporated in a Rinco rotary evaporator, and the salt was further dried in high vacuum for one hour until no more water came off. The salt was then mixed with 25 ml. of 100% phosphoric acid, and this mixture heated at 100° in high vacuum until all the lumps of sodium acetate had disappeared. The acetic acid was collected in a liquid nitrogen-cooled trap, and redistilled onto Drierite. Vapor Fractometer (Perkin-Elmer) analysis showed a negligible water content, and the infrared spectra suggested excellent isotopic purity.[6]

$CH_3(t)COOH$.—The preparation of this material was similar to that of CD_3COOH, except that the starting material was tritiated malonic acid prepared by the exchange of malonic acid with tritiated H_2O (containing 72.5 uc./mmole of tritium).

2. Irradiation of Isotopically Labeled Substances.—Preparation of the acids for irradiation, and the irradiations were carried out as described in the previous paper on deuterated ethanols.[7] The weight of acid in each sample was 3–4 g., and the electron density relative to water was 0.96. The intensity of the γ-source was about 8×10^{17} e.v./g. water-minute (ferrous sulfate dosimeter), and the total dosages were about 1×10^{20} e.v./g. of acid. The infrared spectra of the deuterated acids were observed before and after irradiation (the irradiated materials were vacuum line distilled twice to remove non-volatile products), and were found to be identical. This demonstrates that there was no randomization of the label during the irradiation.

3. Recovery and Analysis of the Radiation Products.—Procedure for this was also as described in the previous paper.[7] After recovery and analysis of the radiolytic hydrogen, a by-pass around the palladium valve was opened and the methane + carbon monoxide fraction was collected, and its volume measured in the gas buret. Hydrogen samples from the deuterated materials were collected in ampules and analyzed mass spectrometrically for deuterium content. The methane fractions from the deuterated acids were similarly collected and analyzed mass spectrometrically for carbon monoxide and the several deuterated methanes. Hydrogen samples from the tritiated materials were collected in an ionization chamber which was filled with methane and the chamber counted on a vibrating reed electrometer. The methane fraction from the tritiated acids was similarly collected and counted. This methane fraction was found to contain only 2–5% of carbon monoxide, and this has been neglected in discussing the results.

(6) Owing to the great breadth of the associated OH stretching band, estimates of the isotopic purity of this acid could not be made from the C–H stretching vibrations but were estimated from the size of the triplet peaks near 2600 cm.$^{-1}$.

(7) J. G. Burr, THIS JOURNAL, **61**, 1477 (1957).

All samples were irradiated at least in duplicate, and all analyses were at least in duplicate.

Results

The data obtained from the irradiation of these labeled molecules is shown in Tables I and II. In Table I, it will be observed that the deuterium contents of the radiolytic hydrogen from the two acids do not add up to 100%, as they should in the absence of any isotope effects. In order to provide a comparison with the deuterium contents to be expected if the hydrogen should originate statistically, the observed deuterium contents have been arbitrarily normalized to total 100%.

TABLE I

HYDROGEN FORMATION FROM DEUTERATED ACETIC ACIDS

Substance	$G_{(H_2)}$[a]	% Deuterium in radiolytic hydrogen: Obsd.	Normalized to 100% basis[b]	Statistical expectation[c]
CH_3COOH	0.45 ± 0.05	...	...	..
CD_3COOH	.30 ± .005	41.4	71.4	75
CH_3COOD	.38 ± .005	16.5	28.6	25

[a] These are the averages and average deviations observed in two or three independent irradiations. [b] These are the observed values multiplied by 1.00/0.579. [c] Evaluated from the number of hydrogen atoms on the CH_3 and the COOH group.

TABLE II

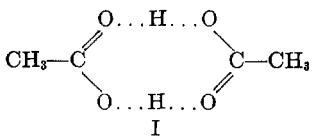
METHANE FORMATION FROM ISOTOPICALLY LABELED ACETIC ACIDS

Substance	Tritium content[a]	G_{CH_4}[b]	Compn. of methane fract.[c]	Tritium content of methane fract.[a]
CH_3COOH	...	3.13 ± 0.15	...	...
CH_3COOD	...	3.15 ± .02	CH_4 —95%	...
			CH_3D— 5%	...
			(CO — 4%)	...
CD_3COOH	...	2.59 ± .01	CD_3H—51%	..
			CD_4 —49%	...
			(CO — 2%)	...
$CH_3COOH(t)$	11.18	3.27	...	0 5
$CH_3(t)COOH$	35.68	3.24 ± .2	...	34.9

[a] In microcuries per millimole. [b] Neglecting the small carbon monoxide content. [c] Mass spectrometer analysis.

Discussion and Conclusions

The radiation chemistry of acetic acid is complicated by the fact that this molecule exists almost entirely as a strongly bonded dimer at room temperature[8] and indeed dimerization is strong up to temperatures of over 150°. This dimer has the structure I. Thus the radiation chemistry of acetic



I

acid is actually the radiation chemistry of the dimer, I. From this point of view, removal of carboxyl hydrogen from the dimer should be more difficult than removal of this hydrogen from the monomer by at least the heat of dissociation.

1. Mechanism of Methane Formation.—The production of methane by a pure molecular process (1) from CH_3COOD should produce pure CH_3D, and from $CH_3COOH(t)$ should produce methane with a tritium content nearly equal to that of the substrate acid. Inspection of Table II shows that this is far from the case. The mixture of methanes obtained from CH_3COOD actually contained only 5% of CH_3D, and the methane from $CH_3COOH(t)$ had only a trace of tritium activity. It can be concluded from this that such a molecular process contributes only a very small amount, if any, to methane formation; and that the radical process (2) is the predominant mechanism for methane formation from these deuterated acids. The presence of the deuterium substituent may have suppressed a molecular process to some extent, although hardly more than by a factor of three; this would permit not more than 15% of methane formation by a molecular process.

It is apparent that the intermediate methyl radicals formed must abstract hydrogen (to form methane) almost entirely from the methyl group of acetic acid molecules. The case observed here thus constitutes the only possible situation from which conclusive data could be obtained by this method, since the formation of methane by a radical process in which the methyl radicals abstracted hydrogen exclusively from the carboxyl hydrogen could not easily be distinguished from the formation of methane by a purely molecular process. The failure of CD_3COOH to produce a correspondingly large percentage of CD_4, or of $CH_3(t)COOH$ to produce methane with a higher tritium content than the substrate molecule can thus be logically ascribed to preferential abstraction of H rather than D or T by the methyl radicals.

The absence of such a molecular process in the results of electron impact on gaseous acetic acid is also strikingly evident in the mass patterns of acetic acid where the peak at 44 (CO^+_2) is very small, and where the peak at 45 ($COOH^+$) corresponding to the radical process is quite large.[9] The significance of this correlation, together with examples of similar correlations, will be discussed in the following paper.

From the effect of added HI + I_2 upon the methane yield in the radiolysis of 16 *M* aqueous acetic acid with 27 Mev. α-particles, Garrison,[4] *et al.*, have concluded that a molecular process contributes about 50% to the formation of methane. One possible reason for this disagreement is that HI + I_2 mixtures are not sufficiently efficient traps for the methyl radicals, perhaps because of regeneration of methane from the methyl iodide *via* reaction with hydrogen atoms.

$$CH_3 + I_2 \longrightarrow CH_3I + I\cdot$$
$$H + CH_3I \longrightarrow CH_4 + I\cdot$$

2. Hydrogen Formation.—Evidence for the mechanism of hydrogen formation in the radiolysis of acetic acid such as was reported in the

(8) J. T. Harris, Jr., and M. E. Hobbs, *J. Am. Chem. Soc.*, **76**, 1429 (1954), have shown that the equilibrium constant, $K = M^2/D$ is 2.5×10^{-4} at 27°. This corresponds to less than 2% monomer in liquid acetic acid. MacDougall (*ibid.*, **58**, 2585 (1936)) has shown that the heat of dissociation is 16,400 cal./mole corresponding to a hydrogen bond energy of about 8 kcal./mole.

(9) G. P. Happ and D. W. Stewart, *ibid.*, **74**, 4406 (1952).

previous paper for ethanol is not so easily forthcoming in the case of acetic acid. Since $G(H_2)$ for CD_3COOH appears to be significantly lower than the values for the other two acids it can be suggested that hydrogen formation is by a radical process in which the hydrogen atoms originate chiefly from the CH_3– group; however, the data are not sufficiently precise to allow the necessary decision that $G(H_2)$ for CH_3COOH and CH_3COOD are exactly the same.

Confirmatory evidence, however, for the radical formation of hydrogen is available from the data on deuterium content of the radiolytic hydrogen (Table I). These data indicate that the radiolytic hydrogen originates almost statistically from the four hydrogen atoms in the molecule. This is contrary to what would be expected from a molecular process which would require hydrogen formation exclusively from the methyl group.

Unfortunately evidence bearing upon this point cannot be obtained from the mass patterns, as was done for ethanol, since the peaks corresponding to hydrogen loss in gaseous acetic acid are too small to be significant.[8]

A CORRELATION BETWEEN MASS SPECTRA AND RADIOLYSIS DATA

BY JOHN G. BURR

Contribution from the Research Department of Atomics International, P. O. Box 309, Canoga Park, Cal.

Received June 19, 1957

Four examples are given of an apparent similarity between the mechanisms of certain types of processes which can be observed in the data from mass spectra and in the data from liquid phase radiolysis of isotopically labeled organic molecules. The possible significance of this correlation is discussed.

Introduction and Data

Among the products formed by the action of electron impact upon organic substances are often materials whose formation can be discussed in terms of two competitive processes—a radical process such as (1) or (4), and a molecular process such as (2) or (3). In many cases it is possible to obtain information both from the nature of the radiolysis products and from the mass spectra of a particular substance about the relative contribution of each of these two kinds of processes to the formation of a particular product such as hydrogen, methane or ethylene from this particular substance. It is desired to point out in this note what appears to be a unique and potentially powerful correlation between the information obtained from mass spectra and the information obtained from radiolysis products about the relative rates of these two types of processes.

There are presently available four examples of the correlation. The first of these is the apparently similar mechanisms for hydrogen formation deduced from both the mass spectra of deuterated ethanols and the radiolysis products of deuterated ethanols. The data for this correlation were presented in the first paper of this series.[1]

The second example is the apparently similar mechanisms for methane formation deduced from both the mass spectra of acetic acid and the radiolysis products of deuterated acetic acids. It was reported in the previous paper[2] that the composition of the deuterated methane mixture produced by radiolysis of CH_3COOD indicated that methane was produced almost exclusively by the radical process (1) rather than by the molecular process (2).

$$CH_3COOH \longrightarrow CH_3 + COOH \quad (1)$$

$$CH_3 + CH_3COOH \longrightarrow CH_4 + CH_2COOH$$

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad (2)$$

These two mechanisms may also be distinguished in the mass pattern of acetic acid. The size of the peak at m/e 45 ($COOH^+$) should be characteristic of mechanism (1) and the size of the peak at m/e 44 (CO_2^+) should be characteristic of mechanism (2). The ratio of these two peak heights should be a measure of the relative contributions of the two mechanisms—this ratio is reported[3] to be $45^+/44^+ = 93.6/4.9$. According to this measure of mechanism, the decomposition of acetic acid by the action of electron impact upon the dilute gas phase proceeds also by a predominant fission into methyl radicals and carboxyl groups.

A third case in which the mechanism for formation of a particular product may be compared in radiolysis and mass spectra is the formation of hydrogen from ethane. By examination of the $H_2/HD/D_2$ ratios in the hydrogen produced by the action of an electron beam upon equal mole fraction mixtures of C_2H_6 and C_2D_6, Dorfman[4] has concluded that not less than 50% of the hydrogen so formed originates *via* a molecular process 3 rather than a radical process 4.

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \quad (3)$$

$$C_2H_6 \longrightarrow C_2H_5 + H \quad (4)$$

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

Analogous information may be obtained from the mass pattern of ethane[5] where it may be assumed that the ratio of the peaks at m/e's 28 and 29 are indicative of the molecular *versus* radical processes in this gas phase electron impact situation. The ratio of these peak heights is reported to be 28/29 = 100/23.8, or a computed 80% preponderance of the molecular process 3.

Finally, Burton and Patrick[6] have reported the

(1) J. G. Burr, THIS JOURNAL, **61**, 1477 (1957).

(2) J. G. Burr, *ibid.*, **61**, 1481 (1957).

(3) Catalog of Mass Spectral Data of the American Petroleum Institute Project 44, Spectrum Serial No. 640.

(4) L. M. Dorfman, THIS JOURNAL, **60**, 826 (1956).

(5) Catalog of Mass Spectral Data of the American Petroleum Institute, Project 44, Spectrum Serial No. 61.

(6) M. Burton and W. N. Patrick, *Disc. Faraday Soc.*, **12**, 88 (1952).