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The Reaction of Carboxylic Acids and Hydrocarbons in a Silent Electric Discharge. I. The Reaction of Acetic Acid with Ethylene[*1]

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In order to ascertain the possibility of telomerization by a silent discharge, a mixture of acetic acid and ethylene was discharged in an ozonizer under various conditions. The α-*C*-alkylation of acetic acid which was expected to result from its discharge-induced reaction with ethylene was not observed; neither propionic acid nor higher carboxylic acids were identified by gas chromatography. However, *n*-butyl acetate was obtained in a good yield. The formation of the acetate can be explained as resulting from the combination of an acetoxy radical with two molecules of ethylene. The yield of the acetate, as well as those of the liquid and gaseous products, increased with a rise in the temperature and in the voltage, with the time, and with a rise in the ratio of ethylene to the acid concentration. Besides this acetate, the liquid products were confirmed to consist of ethyl methyl ketone, acetone, acetaldehyde, hydrocarbons, and ethyl and *n*-propyl acetates. The gaseous products were carbon dioxide, carbon monoxide, C_1—C_4-hydrocarbons, and hydrogen. Judging from the relative concentration of each compound in the reaction products, it may be said that the acetoxy radical ($CH_3COO\cdot$) and the acetyl radical ($CH_3CO\cdot$) are the main intermediates in this reaction system.

No detailed study has been reported on the reaction of an acetic acid-ethylene mixture by light or radiation, not to mention by silent discharge, although a study of the radiolysis[1] of acetic acid has been made.

Acetic acid has an active hydrogen atom, as well as alcohols (primary and secondary), carbonyl compounds, hydrocyanic acid, and mercaptans. Kawamoto[2] has shown that the acrylonitrile and higher cyanides are produced by the reaction of hydrocyanic acid having an α-H with ethylene in a silent discharge, although the author could not find telomers higher than the one-to-one adduct in the discharge-induced reaction of 2-propanol and ethylene.

It would be interesting to ascertain if a silent electric discharge initiates the telomerization of acetic acid and ethylene, and if it can be employed as a means to the direct synthesis of carbonyl compounds or acetates. In the present paper, the author wishes to report the direct formation of acetates in the silent discharge, and to establish, if possible, the optimum conditions for the preparation of these compounds.

[*1] The major part of these research results were presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

1) A. S. Newton, *J. Chem. Phys.*, **26**, 1764 (1957); R. H. Johnsen, *J. Phys. Chem.*, **63**, 2041 (1957).

2) K. Kawamoto, This Bulletin, **41**, 2164 (1968).

Experimental

Materials. The acetic acid, which did not contain any impurities reducing a 0.1% potassium permanganate solution, was purified by column distillation after it had been refluxed over phosphorus pentoxide, while commercial ethylene (research grade) was used without further purification. No impurity was found by gas chromatographical analysis; the analyses of acetic acid and ethylene were performed by means of columns of DEGS (diethylene glycol succinate) and activated charcoal respectively.

Discharge Tube. The discharge tube used is shown in Fig. 1. This tube was a Pyrex tube of the Siemens type[3] with a gap length of 2.5 mm and an effective length of 45 cm. The outside (B) of the discharge tube was filled with water, while the inner tube (A) was filled with a 3% $CuSO_4$ solution. Electrodes (C) were inserted into both (A) and (B).

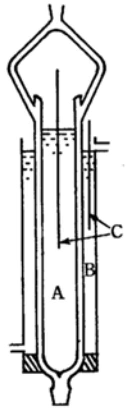

Fig. 1. The used discharge tube.

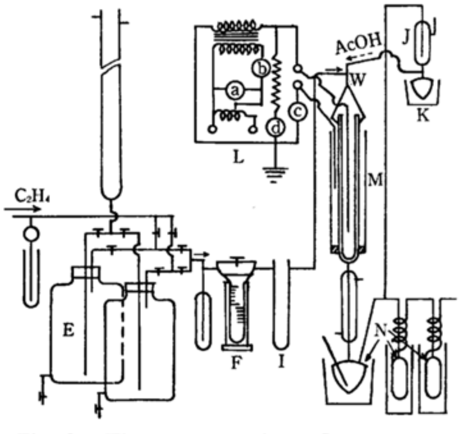

Fig. 2. The apparatus for a flow system.

a) Voltmeter, V b) Ammeter, A
c) Ammeter, mA d) Ammeter, μA

Apparatus and Procedure. The experiment was performed in a flow system. The apparatus is shown in Fig. 2. As soon as acetic acid had been dropped, at regular time intervals, from a dropping funnel (J) into a pot, a heater (K) turned it into vapor, which was then introduced into a discharge tube (M). Ethylene coming from the reservoir (E) was passed through a solid sodium hydroxide tube (I) in order to remove the moisture in the ethylene, which was then introduced into the discharge tube along with the acetic acid vapor. The ethylene flow rate was measured by passing it through a calibrated flowmeter (F). The reaction products that passed through the discharge tube were separated into a condensable part and non-condensable gases by three traps (N) cooled to 0°C. The high tension was applied to the discharge tube from a transformer (L; capacity, 15 kV) which used a 60-cycle alternating current.

Analysis of the Products. The reaction products were identified by comparing their retention times on gas chromatography with those of authentic samples. The non-condensable products were analyzed by gas chromatography (column, 3 m activated charcoal at 100°C; carrier gas, hydrogen). For the analyses of C_3 and C_4-hydrocarbons and of hydrogen, a 3-m column of hexamethylphosphoramide and a 3-m column of molecular sieve-13X were used at 35°C (carrier gas, helium).

The condensable products were confirmed not only by gas chromatography (column, tricresyl phosphate, PEG-6000 and diethylene glycol succinate at 100°C; carrier gas, He), but also by the formation of the derivatives. Thus, ethyl methyl ketone, obtained as a fraction boiling at 80°C, was converted into its semicarbazone and 2,4-dinitrophenylhydrazone,[*2] the melting points of the derivatives being 145.5—146°C and 116.8—117.3°C respectively. They showed no depression of their melting points when mixed with authentic specimens. The quantitative analysis of the liquid products was performed by gas chromatography (column, 3 m, diethylene glycol succinate at 100°C; carrier gas, helium).

Results and Discussion

The experimental conditions and the reaction products are listed in Tables 1 and 2. The main liquid products identified were acetaldehyde, acetone, ethyl methyl ketone, and ethyl, and *n*-propyl and *n*-butyl acetates. The percentage compositions of compounds shown in these tables are the average of three experiments; the fluctuations in the yields of these compounds were less than 1%. The gaseous products which were formed in this reaction were methane, ethane, acetylene, C_3 and C_4-hydrocarbons, carbon monoxide, carbon dioxide, and hydrogen.

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[3] T. Matsuda, K. Oto and K. Sugino, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **79**, 324 (1958).

[*2] The semicarbazone and 2,4-dinitrophenylhydrazone of ethyl methyl ketone were prepared according to the procedure of R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, New York (1956), pp. 218, 219.

TABLE 1. INFLUENCES OF A MOLAR RATIO OF ETHYLENE TO ACETIC ACID ON THEIR DISCHARGE REACTION

Experiment No.	1	2	3	4	5	6
Secondary voltage, kV	11.6	11.6	11.6	11.6	11.6	11.6
current, mA	3.0	2.0	2.2	2.2	2.2	2.2
Temp. of discharge tube						
Inside, °C	88	85	88	88	87	86
Outside, °C	84	84	85	84	78	81
Residence time, hr	6.5	6.5	6	6	6	6
Material						
Acetic acid Amount, g	51.75	52.11	52.33	51.90	52.91	52.26
Velocity, g/hr	8.6	8.7	8.7	8.7	8.8	8.7
Ethylene Volume, *l*	0	7.40	7.80	9.70	11.45	13.50
Velocity, *l*/hr	0	1.23	1.30	1.62	1.91	2.25
Molar ratio (ethylene/AcOH)	0	0.38	0.40	0.49	0.58	0.69
Amount of liquid product, g	1.15	1.89	1.88	1.76	1.89	2.23
Conversion, %*	2.46	2.76	2.80	2.65	2.69	3.15
Composition of liquid product, %**						
Acetaldehyde	6.7	8.2	10.3	8.8	7.1	7.7
Acetone	63.5	11.4	9.2	8.4	9.6	10.2
Ethyl methyl ketone	7.1	11.4	11.9	12.3	12.9	12.2
Ethyl acetate	8.3	7.5	8.0	7.1	7.9	7.4
n-Propyl acetate	1.8	10.8	11.8	12.3	10.7	11.1
n-Butyl acetate	3.5	20.5	17.7	21.8	21.5	23.4
Hydrocarbons	9.1	30.2	31.1	29.3	30.3	28.0

Gaseous products: methane, ethane, acetylene, propane, *n*-butane, 1-butene, carbon monoxide, carbon dioxide and hydrogen.

TABLE 2. INFLUENCES OF DISCHARGE TEMPERATURE, VOLTAGE AND TIME ON THE REACTION BETWEEN ACETIC ACID AND ETHYLENE

Experiment No.	8	9	3	10	11
Secondary voltage, kV	10.3	10.3	11.6	11.6	11.6
current, mA	2.4	1.8	2.2	2.1	2.2
Temp. of discharge tube					
Inside, °C	41	83	88	82	88
Outside, °C	34	86	85	82	83
Residence time, hr	6	6	6	3	9
Material					
Acetic acid Amount, g	51.60	51.38	52.33	52.10	51.11
Velocity, g/hr	8.6	8.6	8.7	8.7	8.5
Ethylene Volume, *l*	8.60	8.95	7.80	10.75	11.40
Velocity, *l*/hr	1.4	1.5	1.3	1.8	1.9
Molar ratio (ethylene/AcOH)	0.44	0.45	0.40	0.55	0.60
Amount of liquid product, g	0.60	0.95	1.88	0.95	2.83
Conversion, %*	1.11	1.61	2.80	1.40	4.21
Composition of liquid product, %**					
Acetaldehyde	3.1	6.5	10.3	8.3	9.1
Acetone	30.9	31.4	9.2	6.9	10.3
Ethyl methyl ketone	4.9	10.0	11.9	12.2	11.6
Ethyl acetate	6.4	8.3	8.0	9.2	8.3
n-Propyl acetate	8.0	6.8	11.8	9.4	12.0
n-Butyl acetate	7.8	20.3	17.7	19.4	16.0
Hydrocarbons	38.9	16.7	31.1	34.6	32.7

Gaseous products: see Table 1.

* The conversion efficiency was given by (grams of reaction product per grams acetic acid used) ×100.

** The yields of each compound were given by (grams of each compound per grams of total reaction product) ×100.

These compounds were obtained in every run (though in the case of the decomposition of acetic acid alone, the acetylene and C_3—C_4-hydrocarbons were not formed). However, the distribution of the products depended upon the voltage of discharge, the residence time, the temperature in the tube, and the molar ratio of the reactants.

Influences of teh Molar Ratio of Ethylene to Acetic Acid on the Yield. In order to check the molar ratio effects on the discharge reaction of acetic acid and ethylene, the reaction was carried out with various ratios of the ethylene to the acetic acid concentration. As may be seen from Experiment Nos. 1—6 in Table 1, the yields of liquid products increased with an increase in the molar ratio of ethylene to acetic acid. However, the distribution of the products depended on the molar ratio of reactants as follows. (1) Acetone was obtained in the highest yield in the absence of ethylene; the acetone yield decreased when acetic acid was mixed with ethylene. Up to the molar ratio of 0.58: 1, the yield decreased almost linearly with an increase in the ratio of ethylene to acetic acid. (2) The yield of ethyl methyl ketone increased at high ratios of ethylene to the acid concentration. These facts seem to indicate that acetone is formed by the combination of an acetyl radical with a methyl radical, and ethyl methyl ketone, by the addition of an acetyl radical to an ethylene, and that the C–OH-bond breaking in the acetic acid excited by the silent discharge is rather preferred in the absence of ethylene.

On the other hand, the yield of acetates identified was lowest in the decomposition of acetic acid; it was favored by high ratios of ethylene to the acid concentration. Thus, it is thought that the acetates are formed *via* an acetoxy radical ($CH_3COO\cdot$), a radical which is produced in large quantities by the free radicals derived from the excited ethylene; the free radicals attack this acetic acid to remove a hydrogen atom in the carboxyl. However, since carbon dioxide was obtained more in the absence of ethylene than in its presence, the high yields of acetates might result from the stabilization of the acetoxy radical in the presence of ethylene. This result also suggests that the decarboxylation is rather more preferred in the discharge decomposition of acetic acid than in the reaction of a mixture of acetic acid and ethylene.

The yield of ethyl acetate was almost the same regardless of the molar ratio of the reactants. The yield of the telomer with $n=2$ (*n*-butyl acetate) increased with an increase in the molar ratio of the ethylene to the acid. Thus, it may be said that the yield of the telomer with $n=2$ is favored by a low ratio of the acetic acid to the ethylene concentration.

Influences of the Discharge Temperature, Voltage, and Time on the Reaction between Acetic Acid and Ethylene. As is shown in Table 2, when the discharge reactions were carried out at 35 and 85°C, under the reaction conditions of a 0.4: 1 molar ratio of ethylene to acetic acid, 10.5 kV, and 6 hr, the yields of the liquid products increased with a rise in the temperature. *n*-Butyl acetate (1:2 telomer) was obtained in an especially high yield when the ozonizer was kept "warm." This fact indicates that the telomerization of this sort is much affected by the discharge temperature.

On the other hand, the yields of the liquid products increased at a high voltage of discharge; the yields of all the carbonyl compounds except acetone, and of the acetates increased (the acetone yield, on the other hand, decreased very much). This suggests that the addition reaction occurs predominantly at a high tension.

Further, it has been found that increasing the residence time increases not only the reaction rate but also the yields of all the carbonyl compounds, including acetone, and of the acetates.

Thus, it has become apparent that the yields of the liquid and gaseous products increase with a rise in the temperature, the voltage, and the time, and at high ratios of the ethylene to the acetic acid concentration (a high yield of the telomer with $n=2$, *n*-butyl acetate, is especially favored by such a ratio).

Besides *n*-butyl acetate, liquid products were confirmed to consist of ethyl methyl ketone, acetone, acetaldehyde, and ethyl and *n*-propyl acetates, plus hydrocarbons. The gaseous products were C_1—C_4-hydrocarbons, carbon monoxide and dioxide, and hydrogen.

Judging from the relative concentration of each compound in the reaction products, it may be said that the acetoxy radical ($CH_3COO\cdot$) and the acetyl radical ($CH_3CO\cdot$) are the main intermediates in this reaction system.

The Assumed Radicals and Reaction Scheme. The characteristic of the action of silent discharge on a compound seems to be the electronic excitation of the molecule. Some of the molecules may be transformed by inelastic collisions into vibrationally-excited molecules. The activated molecules thus formed are considered to change into radicals or atoms, and into a very small amount of ionized molecules, as has been reported by many workers.[4] The radicals which are assumed to be formed from acetic acid under a silent discharge and a part of the postulated reaction scheme are shown in Table 3.

These precursor radicals, II—IV, might be

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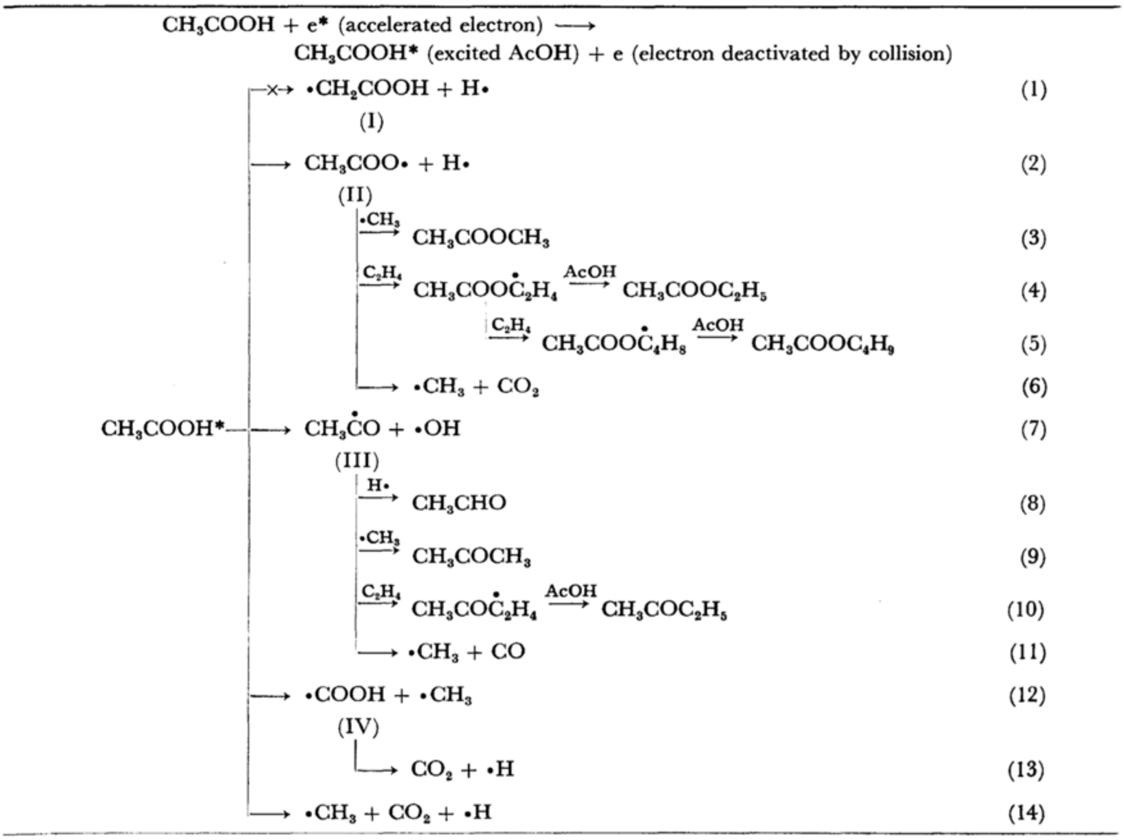
[4] S. C. Lind and G. R. Schultze, *J. Phys. Chem.*, **42**, 547 (1938); H. Winer and M. Burton, *J. Am. Chem. Soc.*, **75**, 5815 (1953); J. C. Devins and M. Burton, *ibid.*, **76**, 2618 (1954); E. Inoue, *Denki Kagaku (J. Electrochem. Soc. Japan)* **23**, 574 (1955); S. Takahashi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **79**, 132 (1958).

TABLE 3. THE ASSUMED RADICALS AND REACTION SCHEME



formed not only by the reactions shown in this table, but also by various reactions between acetic acid and the various radicals formed. The Radical (I) seems not to be derived from acetic acid excited by the silent discharge (even if the radical were formed, the radical would be too labile to exist), since propionic acid, butyric acid, and higher carboxylic acids were not identified by gas chromatography.

When acetic acid alone was discharged in an ozonizer, acetone and carbon monoxide were obtained in good yields. Accordingly, the C–OH-bond breaking in acetic acid (Eq. (7)) seems to occur rather preferably in the case of the decomposition of the excited acetic acid.

In the present reaction system, the (6), (13) and (14) processes seem to be those for forming carbon dioxide, but the processes to give CO_2 may not necessarily be these three, because Adams *et al.*[5] have shown, by the use of a radical scavenger, that 20% of the methane obtained in the radiolysis of acetic acid passes through the "molecule" process, $CH_3COOH^* \rightarrow CH_4 + CO_2$. Moreover, Ausloos and Steacie[6] have shown that 10% of the methane produced was derived from the dissociation of the acetic acid vapor excited by light.

Comparison with Peroxide-, Light-, and Gamma-Ray-Induced Reactions. The liquid products obtained in the decomposition of the acetic acid excited by the silent discharge are similar to those obtained in the radiolysis of acetic acid as shown by Bach,[7] Johnsen,[1] and Newton.[1] However, Burr[8] has shown that, in each radiolysis of the deuteriated and tritiated acetic acids, CD_3COOH and CT_3COOH, the methane and hydrogen produced were formed through the following processes:

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[5] G. E. Adams, J. H. Baxendale and R. P. Sedgwick, *J. Phys. Chem.*, **63**, 854 (1959).

[6] P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1530 (1955).

[7] Bach showed that the *G*-value of the acetone formed in the radiolysis of acetic acid vapor was 0.45; N. Bach, *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, United Nations, New York, **7**, 538 (1956). In addition, Johnsen showed that the *G*-values of the gaseous products were 0.35 (H_2), 3.34 (CH_4), 0.62 (C_2H_6), 0.37 (CO), and 6.0 (CO_2). Further, Newton has reported that, besides these compounds, acetaldehyde and methyl acetate are obtained in such a reaction system.

$$\cdot CH_3 + CH_3COOH \rightarrow CH_4 + \cdot CH_2COOH$$
$$\cdot H + CH_3COOH \rightarrow H_2 + \cdot CH_2COOH$$

Namely, Burr[8] proposed the formation of the $\dot{C}H_2$-COOH radical. In addition, Roland and Harmon,[9] and Coffman[10] showed that the product was $H(C_2H_4)_nR'COOH$, in which R′ is R less H; this product was not formed by the discharge when a saturated organic acid (RCOOH) with an α-H is heated to 70—80°C with ethylene and a catalyst such as benzoyl peroxide under pressure at 895—950 atm.

It has been reported by Thomas *et al.*[11] that the radical from ethylene in the electrical discharge is a vinyl radical, and that it is produced by breaking a carbon-hydrogen bond. However, since the formations of vinyl acetate and methyl vinyl ketone were not observed, the vinyl radical is considered not to be formed here; the carbon-hydrogen bond in ethylene is not broken to give the vinyl radical, but is activated to give acetylene and 1-butene. These compounds were obtained in the gaseous products.

The main conclusion to be drawn from these results is that, by using a high-frequency current to energize the ozonizer, the nature of the reaction products can be controlled by controlling the experimental conditions. In one case the major product was acetone, and in another, *n*-butyl acetate.

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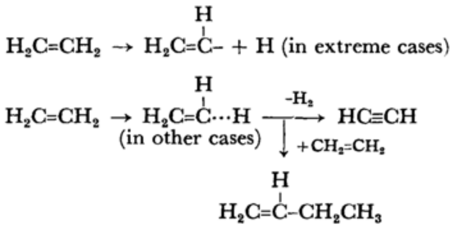
[8] J. G. Burr, *J. Phys. Chem.*, **61**, 1481 (1957).

[9] J. R. Roland and J. Harmon, U. S. Pat. 2433015 (1947); *Chem. Abstr.*, **42**, 2268 (1948).

[10] D. D. Coffman, U. S. Pat. 2433016 (1947); *Chem. Abstr.*, **42**, 2456 (1948).

[11] Thomas *et al.* showed that the processes in the decomposition of ethylene excited by the silent discharge were as follows:



where C···H indicates an activated C–H-bond; C. L. Thomas, G. Egloff and J. C. Morrell, *Chem. Revs.*, **28**, 1 (1941).