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The Reaction of Carboxylic Acids and Hydrocarbons in a Silent Electric Discharge. II. The Reactions of Ethylene with Methyl Acetate and with Acetic Anhydride[*1]

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The present study was undertaken in order to ascertain the difference, if any, in the chemical behavior of methyl acetate and acetic anhydride submitted to a silent discharge between that in the presence and that in the absence of ethylene. (1) In the reaction of methyl acetate without ethylene, the main products were methanol, diacetyl, liquid hydrocarbons, formaldehyde, methane, carbon dioxide, carbon monoxide, and hydrogen. Although the methanol yield was almost the same, regardless of the presence or absence of ethylene, the yields of the hydrocarbons, all the carbonyl compounds, and of *n*-butyl acetate increased in the presence of ethylene. The great quantity of methanol produced might indicate that C–OCH_3-bond breaking in the methyl acetate occurs preferably upon the discharge. (2) With acetic anhydride, on the other hand, acetaldehyde, acetone, ethyl acetate, ethyl methyl ketone, diacetyl, hydrocarbons, carbon monoxide, carbon dioxide, and hydrogen were obtained as the main products. The yields of acetone and diacetyl decreased remarkably in the presence of ethylene, while the yields of hydrocarbons, ethyl methyl ketone, *n*-butyl methyl ketone, and of *n*-butyl acetate increased. The $CH_3COO\cdot$ and $CH_3CO\cdot$ radicals are thought to be the main intermediates in this reaction. The formation of *n*-butyl acetate and of *n*-butyl methyl ketone in the presence of ethylene can be explained on the basis of the telomerization of ethylene initiated by these radicals.

In the previous paper,[1)] the reaction between acetic acid and ethylene by a silent discharge was studied. The α-C-alkylation which has been known to take place in the reaction[2,3)] of a saturated organic acid with ethylene in the presence of benzoyl peroxide at 70—80°C did not occur when there was the discharge. Instead, the formations of ethyl and *n*-butyl acetates and of carbonyl compounds (acetone, ethyl methyl ketone, *etc.*) were observed in the discharge reaction. These observations were explained in terms of the telomerization of ethylene initiated by the $CH_3COO\cdot$ and $CH_3CO\cdot$ radicals which were formed from CH_3COOH under the discharge.

One of the purposes of the present study was to ascertain whether the $CH_3COO\cdot$ and $CH_3CO\cdot$ radicals are formed as the main intermediate also in the decompositions of methyl acetate and acetic anhydride under a silent discharge, and to check whether or not a similar telomerization occurs under the present reaction conditions.

Experimental

Materials. The methyl acetate was purified by washing it with a 10% sodium chloride solution three times, refluxing it over quick lime, and then distilling it through a column. The acetic anhydride was purified by column distillation *in vacuo* after it had been allowed to stand for 2—3 days with a small amount of sodium. Commercial ethylene was used without purification. No impurity was found in these reagents by gas-chromatographical analysis. For the analyses of methyl acetate and acetic anhydride and of ethylene, a 3-m column of DEGS (diethylenglycol succinate) and a 3-m column of activated charcoal respectively were used at 100°C.

Apparatus and Procedure. All the experiments were performed in a flow system. The apparatus and the procedure were similar to those previously reported.[1)]

Analysis of the Products. The non-condensable gases produced were identified by comparing their retention times on gas chromatography with those of authentic samples. (Columns of activated charcoal, hexamethylphosphoramide, and molecular sieve-13X were used.) The gaseous products were not determined quantitatively.

The condensable products were confirmed not only by gas chromatography (columns; tricresyl phosphate, DEGS, PEG-6000, and silicon DC-550 at 120°C; carrier gas: He), but also by the formation of their derivatives. Thus, ethyl methyl ketone, obtained as a fraction boiling at 80—82°C, and acetone (bp 56—

[*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) T. Hiraki, This Bulletin, **42**, 1981 (1969).

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

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

57°C) were converted into their semicarbazones,*2 the melting points of the derivatives being 146—146.5°C and 186.5—187°C respectively. They showed no depression in their melting points when mixed with authentic specimens. The quantitative analysis of the liquid products was performed by gas chromatography (column: a 3-m column of PEG-6000 and a 3-m column of DEGS, at 120°C).

Results and Discussion

When the discharge reactions of methyl acetate or acetic anhydride with ethylene were carried out in a Pyrex tube of the Siemen type under the conditions shown in Table 1 (helium was used in the case of the reaction without ethylene), a large number of compounds were obtained in every run. Among these, the identified compounds are summarized in Table 2. The percentage compositions of products shown in this table are the averages of three experiments; the fluctuations in the yields of these compounds were less than 1%.

I. The Reaction of Methyl Acetate. *Influence of Ethylene on the Discharge Reaction of Methyl Acetate.* As may be seen from Experiments No. 21 and 22 in Table 2, a large number of compounds were formed along with methanol, the major product in the reaction of methyl acetate with ethylene; acetaldehyde, diacetyl, ethyl methyl and methyl vinyl and *n*-butyl methyl ketones, *n*-propyl and *n*-butyl acetates, liquid hydrocarbons, formaldehyde, C_1—C_4-hydrocarbons, carbon dioxide, carbon monoxide, and hydrogen were all detected.

Most of these compounds were also formed in the silent discharge-induced reaction of methyl acetate without ethylene (Exp. No. 20). However, the distribution of the products was different from that in the reaction without ethylene: (1) While the methanol yield was scarcely affected at all by the presence of ethylene, the yields of all the carbonyl compounds and acetates increased in the presence of ethylene. (2) The propylene, *n*-butane, 1-butene, and 1,3-butadiene in the gaseous products were formed only in the presence of ethylene. (3) Influences of the molar ratio of ethylene to methyl acetate on the conversion efficiency (percentage of grams of the reaction product per grams of methyl acetate used) and the products pattern were not recognized in the region of the ratios from 0.6 : 1 to 0.9 : 1.

The increase in methyl vinyl ketone in the presence of ethylene may be due to the combination of a $CH_3CO\cdot$ radical with a vinyl radical, which has been reported to be formed from ethylene in the electrical discharge.4) The formation of acetylene, 1-butene, and 1,3-butadiene also supports the idea of the formation of the intermediate vinyl radical. On the other hand, the formation of *n*-butyl methyl ketone and *n*-butyl acetate in the presence of ethylene suggests telomerization of ethylene involving the $CH_3CO\cdot$ and $CH_3COO\cdot$ radicals.

The Assumed Radicals and the Reaction Scheme. It is believed that most of the products in the discharge-induced reaction can be explained on the basis of known free redical processes. Since many

TABLE 1. CONDITIONS OF THE REACTIONS OF ETHYLENE WITH METHYL ACETATE, AND WITH ACETIC ANHYDRIDE IN A SILENT DISCHARGE

Reaction system		Methyl acetate			Acetic anhydride		
Experiment No.		20	21	22	30	31	32
Materials used							
a) AcOMe or Ac_2O	Amount, g	46.60	46.28	47.16	45.05	45.82	53.60
	Velocity, g/hr	7.8	7.7	7.9	7.5	7.6	8.9
b) Ethylene*	Volume, *l*	0	8.35	12.55	0	7.35	11.70
	Velocity, *l*/hr	—	1.39	2.09	—	1.22	1.92
Molar ratio (b/a)		0	0.6	0.9	0	0.4	0.6
Second. voltage, kV		11.6	11.6	11.6	11.6	11.6	11.6
Second. current, mA		0.2	2.5	2.7	3.2	2.0	2.0
Temp. of discharge tube							
Inside, °C		80	88	87	86	88	88
Outside, °C		84	85	80	82	81	84
Discharge time, hr		6	6	6	6	6	6

* Exp. Nos. 20 and 30 were carried out in a stream of helium (velocity, 1.33 and 1.26 *l*/hr respectively) instead of ethylene.

[*2] The semicarbazones of ethyl methyl ketone and acetone 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), p. 218.

4) C. L. Thomas, G. Egloff and J. C. Morrell, *Chem. Revs.*, **28**, 1 (1941).

TABLE 2. THE REACTION PRODUCTS

Experiment No.	20	21	22	30	31	32
Amount of liquid products, g	6.22	6.15	5.81	1.63	1.51	1.57
Conversion, %*	10.99	13.29	12.32	3.62	3.29	2.92
Composition of liquid products, %**						
Methanol	94.6	81.1	81.9	—	—	—
Acetaldehyde	0.3	1.1	0.9	6.9	7.4	7.1
Acetone	—	—	—	50.9	27.3	12.5
Ethyl methyl ketone	0.5	0.7	0.8	14.3	17.1	25.5
n-Butyl methyl ketone	—	0.1	0.1	—	3.3	2.8
Methyl vinyl ketone	1.0	4.1	3.0	—	—	—
Diacetyl	1.6	1.0	1.1	12.4	5.6	7.1
Ethyl acetate	***	***	***	6.5	7.7	6.8
n-Propyl acetate	—	1.3	1.1	—	—	—
n-Butyl acetate	—	0.1	0.3	—	4.5	5.7
Hydrocarbons	1.5	7.2	8.1	7.2	27.1	32.5
The others	0.5	3.3	2.7	1.8	—	—

Gaseous products****: Methane, Ethane, Acetylene, Propane, Propylene, Butane, 1-Butene, 1,3-Butadiene, Carbon monoxide, Carbon dioxide, Hydrogen, and Formaldehyde.

* The conversion efficiency was given by (grams of reaction product per grams of methyl acetate or acetic anhydride used) × 100.

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

*** Ethyl acetate might has been produced, but this product could not be identified because of interference by a large peak of methanol.

**** Formaldehyde was only obtained in the reaction of methyl acetate, and also hydrocarbons higher than C_3 were not obtained in Exp. Nos. 20 and 30.

workers[5] have reported that the extent of the formation of ionized molecules in the discharge reaction is very small, the possible ion-molecule reactions which might explain the products will not be considered in this discussion.

Primary Processes. The possible homolytic cleavage of methyl acetate can be shown as follows:

$$\begin{aligned} CH_3COOCH_3^* &\rightarrow CH_3CO\cdot + \cdot OCH_3 && \text{(I)} \\ &\rightarrow \cdot CH_2COOCH_3 + H\cdot && \text{(II)} \\ &\rightarrow CH_3COO\dot{C}H_2 + H\cdot && \text{(III)} \\ &\rightarrow CH_3COO\cdot + \cdot CH_3 && \text{(IV)} \\ &\rightarrow \cdot CH_3 + \cdot COOCH_3 && \text{(V)} \\ &\rightarrow 2\cdot CH_3 + CO_2 && \text{(VI)} \end{aligned}$$

where $CH_3COOCH_3^*$ denotes a methyl acetate excited by the discharge.

The high yield of methanol in the reaction of methyl acetate without ethylene by the silent discharge indicates that Step I is the most probable primary process. This cleavage has been proposed as a major process in the radiolysis of methyl acetate also.[6]

Rust *et al.*[7] have shown that the dissociation of the $\cdot OCH_3$ radicals formed in the vapor-phase decomposition of methyl *t*-butyl peroxide ($Me_3C\cdot O\cdot O\cdot Me$) in the presence of cyclohexene was no more than 0.2%; 99.8% of the radical produced was converted into methanol. Evidence for the stability of $\cdot OCH_3$ radicals has also been reported by Shteen *et al.*[8] On the other hand, the presence of carbon monoxide in the gaseous products indicates that another radical in Step I, $CH_3CO\cdot$, immediately decomposed, as has been proposed to be the case in photolysis[9] and radiolysis.[6] As a result, the yields of carbonyl compounds may be low. Thus, at least to some extent, process I may be written:

$$CH_3COOCH_3^* \rightarrow \cdot CH_3 + CO + \cdot OCH_3$$

Although the presence of hydrogen in the gaseous products may be good evidence for the occurrence of processes II and III, the formation of the $\cdot CH_2COOCH_3$ radical (process II) is apparently of minor importance in view of the fact that no

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[5] S. C. Lind and G. R. Schultz, *J. Phys. Chem.*, **42**, 547 (1938); H. Wiener 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**, 76 (1955).

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

[7] F. F. Rust, F. H. Seibold and W. E. Vaughan, *ibid.*, **72**, 338 (1950).

[8] Shteen *et al.* have shown that the stability of $\cdot OCH_3$ radicals may be due to the geometrical configuration of H and O in the radical and to the endothermic dissociation process of the radicals; N. YA Shteen, N. YA Chernyak, V. L. Antonovskii and A. F. Revzin, *Zh. Fiz. Khim.*, **28**, 240 (1954).

methyl propionate and butyrate were obtained.

It can be thought that carbon dioxide, ethane, and methane are formed *via* three processes, IV, V, and VI. The IV and V processes have previously been proposed in radiolysis.[6]

Secondary Reactions. The possible ways of the production of methanol are thought to be as follows:

$$\cdot OCH_3 + CH_3COOCH_3 \rightarrow CH_3OH + R\cdot \qquad (1)$$

$$2\ \cdot OCH_3 \rightarrow CH_3OH + HCHO \qquad (2)$$

Wijnen has reported that methanol production *via* reaction (1) occurs mainly in the photolysis of CH_3COOCH_3 over the temperature range from 29 to 217°C,[9] and that a similar tendency is observed also in the photolysis of i-$C_3H_7OOCC_2H_5$ at 29—65°C.[10] From the above data, most of the methanol here can be thought to be formed through reaction (1).

The methanol yield was almost the same both in the presence and in the absence of ethylene. This might indicate that most of the methoxy radicals abstract the hydrogen atom from methyl acetate rather than add to the ethylene (little or no ethyl methyl ether or butyl methyl ether was obtained). Rust *et al.*[7] have also shown that $\cdot OCH_3$ radicals add to cyclohexene scarcely at all.

The formations of methyl vinyl ketone and n-butyl acetate in the presence of ethylene are thought to occur *via* the following reactions:

$$CH_3CO\cdot + \cdot CH{=}CH_2 \rightarrow CH_3COCH{=}CH_2 \qquad (3)$$

$$CH_3COO\cdot + CH_2{=}CH_2 \rightarrow CH_3COOCH_2\dot{C}H_2 \qquad (4)$$

$$CH_3COOCH_2\dot{C}H_2 + CH_2{=}CH_2 \rightarrow CH_3COO\dot{C}_4H_8 \qquad (5)$$

$$CH_3COO\dot{C}_4H_8 + CH_3COOCH_3 \rightarrow CH_3COOC_4H_9 + R\cdot \qquad (6)$$

Some of the $CH_3CO\cdot$ or $CH_3COO\cdot$ radicals (though most of these radicals may decompose immediately) may react on a vinyl radical and/or ethylene. The possibility that these reactions occur in a silent discharge has been discussed in connection with the reaction of acetic acid with ethylene previously studied.[1]

Comparison with Radiolysis. The products that were obtained in the decomposition of the methyl acetate excited by the silent discharge were similar to those obtained in the rediolysis;[6] Ausloos and Trumbore have shown that the G-values of the gaseous products are 2.14 (H_2), 1.76 (CH_4), 0.43 (C_2H_6), 2.68 (CO), 1.10 (CO_2), and 0.034 (CH_3OCH_3), and that methanol is the major liquid product.

Interestingly, however, the γ-ray-induced reaction of methyl formate with ethylene[11] has been found to produce the esters, $H(CH_2CH_2)_n\ COOCH_3$ (n=6.9 on the average), which were not formed by the discharge reaction.

II. The Reaction of Acetic Anhydride. *Influence of Ethylene Addition on the Discharge Reaction of Acetic Anhydride.* As may be seen from Experiments No. 31 and 32 in Table 2, the main liquid products in the silent discharge-induced reaction of acetic anhydride with ethylene were acetaldehyde, acetone, ethyl methyl and n-butyl methyl ketones, diacetyl, and ethyl, n-propyl and n-butyl acetates. The gaseous products were C_1—C_4-hydrocarbons, carbon dioxide and monoxide, and hydrogen.

Most of these compounds were also obtained in the reaction without ethylene (Exp. No. 30), but the distribution of the products was different from that in the reaction without ethylene; also, it was influenced by the molar ratio of the reactants: (1) The highest yields of acetone and diacetyl were in the absence of ethylene; the yields of these products decreased almost linearly with a rise in the ratio of the ethylene to the acetic anhydride concentration. Especially, the acetone yield decreased remarkably at a high ratio. (2) In the presence of ethylene, the yield of ethyl methyl ketone increased. Further, n-butyl acetate and n-butyl methyl ketone, which were not formed in the reaction without ethylene, were obtained; their yields increased slightly with an increase in the ratio of the ethylene to the acetic anhydride concentration.

These results suggest that, in the presence of ethylene, most of the $CH_3CO\cdot$ radicals which did not decompose add to ethylene rather than recombine with the methyl radical. The production of n-butyl acetate in the presence of ethylene may be good evidence for the formation of the $CH_3COO\cdot$ radical as an intermediate.

The Reaction Occurring in the Silent Discharge. The discharge-induced reaction of acetic anhydride is presumed to be chiefly a radical reaction, also. Thus, on the basis of the products, the assumed radicals and a part of the postulated reaction scheme may be formulated as follows:

$$(CH_3CO)_2O^* \rightarrow CH_3CO\cdot(A) + CH_3COO\cdot(B) \qquad (7)$$

$$\rightarrow 2\ \cdot CH_3(C) + CO_2 + CO$$

$$(\text{or } C_2H_6 + CO_2 + CO) \qquad (8)$$

$$\rightarrow 2\ CH_3CO\cdot + \cdot O\cdot(D) \qquad (9)$$

where $(CH_3CO)_2O^*$ represents the acetic anhydride excited by the discharge.

The evidence for the occurrence of the A and B radicals in this reaction system has been already

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9) M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 710 (1957); *ibid.*, **28**, 271 (1958).

10) M. H. J. Wijnen, *J. Am. Chem. Soc.*, **82**, 1847 (1960).

11) A. D. Petrov, G. I. Nikisin and V. D. Vorob'ev, *Fette u. Seifen*, **59**, 1023 (1957); *Chem. Abstr.*, **52**, 7141 (1958).

discussed. Moreover, the presence of carbon monoxide and dioxide in the gaseous products may be clear evidence of the production of the excited $CH_3CO\cdot$ and $CH_3COO\cdot$ radicals, which decompose before taking part in any reactions. It has been demonstrated by many workers[9,12,13] that these radicals are rather unstable. Thus, the reactions (7) and (8) are thought to be the most probable primary processes.

The Mechanisms of the Formations of n-Butyl Acetate and n-Butyl Methyl Ketone. The one-to-two adducts, such as *n*-butyl acetate and *n*-butyl methyl ketone, were obtained in the reaction of acetic anhydride with ethylene under the silent discharge. The formation of these telomers may be presented as follows:

$$R\cdot + CH_2{=}CH_2 \rightarrow RCH_2\dot{C}H_2 \qquad (10)$$

$$RCH_2\dot{C}H_2 + CH_2{=}CH_2 \rightarrow R(CH_2)_3\dot{C}H_2 \qquad (11)$$

$$R(CH_2)_3\dot{C}H_2 + AH \rightarrow R(CH_2)_3CH_3 + A\cdot \qquad (12)$$

where $R\cdot$ represents a $CH_3COO\cdot$ or $CH_3CO\cdot$ radical and where AH is any hydrogen donor (most AH's are probably the hydrocarbons produced).

Comparison with Pyrolysis. Szwarc and Murawski[14] have shown that the thermal decomposition of acetic anhydride is not a radical reaction, but a "molecular" process, because equimolecular amounts of ketene and acetic acid are obtained in the pyrolysis of acetic anhydride in a stream of toluene vapor. However, the possibility of this process is not thought to be important in the present study because such products were not obtained.

This difference in reaction paths is not surprising. It has been proposed by Thomas *et al.*[4] that there are essential differences between thermal activation and electrical activation. In the former energy must be put into the entire aggregation of molecules, but in the latter the electron collides with the bonding electrons.

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[12] R. W. Hummel, *Trans. Faraday Soc.*, **56**, 234 (1960).

[13] L. Jaffe, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957); P. Ausloos, *Can. J. Chem.*, **36** 383 (1958); W. A. Pryor, "Introduction to Free Radical Chemistry," Prentice-Hall, New Jersey (1966), p. 23.

[14] M. Szwarc and J. Murawski, *Trans. Faraday Soc.*, **47**, 269 (1951).