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The Reaction of Alcohols and Hydrocarbons in a Silent Electric Discharge. I. The Decomposition of 2-Propanol by the Discharge[*1]

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The reaction of 2-propanol under a silent electric discharge was studied using two kinds of discharge tubes. One was Siemen's tube, which was used for investigating a silent discharge decomposition of 2-propanol. The other was a special tube that had one side of the walls made of copper or its salts; it was used for studying the effects of the wall on the decomposition. The main liquid products were acetaldehyde, acetone, *dl*-2-butanol, 2-methyl-2-propanol, 2-methyl-2-butanol, and hydrocarbons. The gaseous products were methane, C_2—C_4-hydrocarbons, carbon monoxide, carbon dioxide, and hydrogen. These components were obtained in every run, regardless of the type of tube used. However, the distribution of the products varied with the sort of tube. The formation of 2-methyl-2-butanol can be explained by the addition of a 1-hydroxyisopropyl radical with the ethylene produced; the only product formed by adding this radical to ethylene was the one-to-one adduct. By replacing one side of the glassy walls with a wall of a glass-filter-packed copper or its salts, the yield of 2-methyl-2-propanol was increased relatively, and those of 2-methyl-2-butanol and *dl*-2-pentanol were decreased.

Kawamoto *et al.*[1] found that acrylonitrile and higher cyanides were produced by the reaction of prussic acid with ethylene in a silent electric discharge. The higher cyanides seem to be formed by a chain telomerization.

A similar telomerization may also occur in the discharge reaction of 2-propanol and ethylene, considering Urry's[2] research on the peroxide- and light-induced additions of several alcohols to olefins, and the fact[3,4] that the α-C-alkylations of primary and secondary alcohols result not only from peroxide- or light-induced reaction, but also from gamma-ray irradiation.

It would be interesting to ascertain if a silent electric discharge initiates the telomerization. In the present paper, preliminarily, the author wishes to report some observations on the chemical behavior of 2-propanol submitted to silent discharge, including a study of the effects on the reaction of a wall made of copper or its salts.

Experimental

Material. 2-Propanol was purified by column distillation after it had been refluxed over potassium carbonate. No impurity was found by gas chromatographical analysis using a 3-m column of PEG-6000.

Packing. The packing material shown in Table 1 was prepared by the method described in Kawamoto's[5] paper.

Discharge Tubes. The discharge tubes used are shown in Fig. 1-a. Two kinds of tubes, here simply noted as tube 1 and tube 2, were used.

Tube 1 was a Pyrex tube of the Siemen type[6] 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).

Tube 2 was a Pyrex tube with a glass filter which had an effective length of 30 cm, an outside diameter of 2 cm, and a space gap 2.5 mm long. The outside (B) of the discharge tube and a glass filter (D) were filled with water and 5 g of the packing material respectively. Electrodes (C) were inserted into both (B) and (D).

Apparatus and Procedure. The experiment was performed by using the flow system and the reflux system. The apparatus for the flow system and the reflux system are shown in Figs. 2 and 3. The reduced copper for packing was prepared by passing purified

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[*1] The major part of this research was presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

1) K. Kawamoto and S. Tsutsumi, Preprints for the 18th Annual Meeting of the Chemical Society of Japan (1965), p. 173.

2) W. H. Urry, F. W. Stacey, E. S. Huser and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).

3) T. Kurihara and H. Hotta, This Bulletin, **37**, 1448 (1964).

4) K. Hirota and M. Hatada, *ibid.*, **34**, 1644 (1961).

5) K. Kawamoto, *ibid.*, **34**, 161 (1961).

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

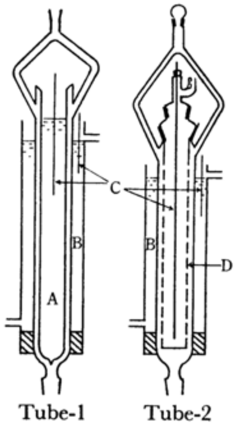

Fig. 1-a. The used discharge tubes.

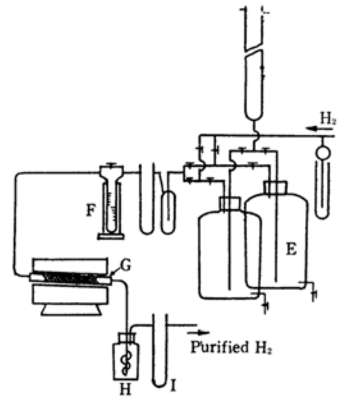

Fig. 1-b. Apparatus for purifying hydrogen.

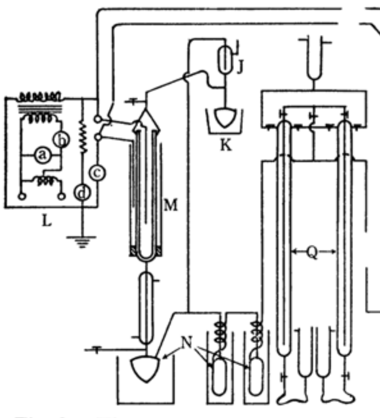

Fig. 2. The apparatus for a flow system.
- a) Voltmeter, V
- b) Ammeter, A
- c) Ammeter, mA
- d) Ammeter, μA

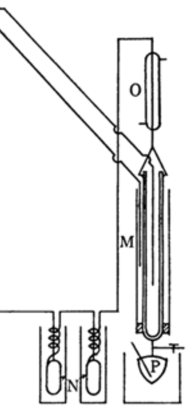

Fig. 3. The apparatus for a reflux system.

hydrogen on copper salt for 3—5 hr and at a velocity of 1.0—1.4 *l*/hr through the filter heated to 180°C. The apparatus for purifying hydrogen is illustrated in Fig. 1-b. Hydrogen coming from the reservoir (E) was passed through a tube (G) containing heated copper gauze in order to remove the oxygen in the hydrogen, and then through a bottle (H) containing a 30% sodium hydroxide solution and a solid sodium hydroxide tube (I). The hydrogen flow rate was measured by passing it through a calibrated flowmeter (F).

In the case of the flow system, as soon as the 2-propanol had fallen at a regular velocity from a dropping funnel (J) into a pot, a heater (K) turned it into vapor, which was then introduced into a discharge tube (M). The reaction products that passed through the tube were separated into a condensable part and non-condensable gases by three traps (N) cooled to 0°C.

In the case of the reflux system, 2-propanol in a still pot (P) was vaporized by heating it to 110°C; the vapor was then passed through the discharge tube (M). The reaction products passed through the discharge field were preliminarily separated into a condensable part and non-condensable gases by a condenser (O) kept at 55°C. The condensable products came back to the still pot again. The non-condensable part was further separated from the condensable products by two traps (N) cooled at 0°C. The volume of non-condensable gas was measured by a calibrated gas holder (Q).

The high tension was applied to the discharge tube from a transformer (L; capacity, 15 kV) which used a 60-cycle alternating current.

Analyses. 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 HMPA (Hexamethylphosphoric triamide) and a 3-m column of molecular sieve-13X were used at 35°C (carrier gas, helium).

The condensable products were identified not only by gas chromatography (column, tricresyl phosphate, PEG-6000 and silicon DC-550 at 100°C; carrier gas, helium), but also by derivatization. Thus, 2-methyl-2-propanol, obtained as a fraction boiling at 81—82°C, and *dl*-2-butanol (bp 99—100°C) were converted into their 3,5-dinitrobenzoates,[*2] the melting points of the derivatives being 140—141°C and 75—76°C respectively. They showed no depression of the melting points when mixed with authentic specimens. The quantitative analysis of the liquid products was performed by gas chromatography (column, 3 m, PEG-6000 at 100°C; carrier gas, He).

Results and Discussion

The decomposition of 2-propanol was performed under the experimental conditions shown in Table 1; the reaction products which have been identified are listed in Table 2. The subscripts A and B in these tables indicate a flow system and a reflux

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[*2] The 3,5-dinitrobenzoates of 2-methyl-2-propanol and *dl*-2-butanol were prepared according to the procedure of Shriner *et al.*: 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. 212.

TABLE 1. EXPERIMENTAL CONDITIONS

Exp. No.	1		2		3		4		5		6	7
System of process	A	B	A	B	A	B	A	B	A	B	B	A
Packings*	$Cu(OH)_2$		Reduced Cu-1		$CuCO_3 \cdot Cu(OH)_2$		Reduced Cu-2		Cu		None	None
Second. voltage, kV	15	15	15	15	15	15	15	15	15	15	13.5	15
current, mA	0.9	0.7	0.5	0.8	0.5	0.4	0.5	0.4	0.9	0.4	4.7	2.8
Temp. of discharge	85	85	85	85	85	85	85	85	85	85	15	85
tube, °C											in, 32	85
Discharge time, hr	4	4	4	4	4.5	4	4	4	4.5	4	9	4.5
Material:												
2-Propanol												
Amount, g	38.56	38.88	38.85	38.98	38.68	38.92	38.94	38.97	38.60	38.97	38.78	36.99
Velocity, g/hr	9.65	—	9.71	—	8.60	—	9.72	—	8.58	—	—	8.22

* Symbol of reduced Cu-1 or -2 means the reduced copper that prepared by treating copper (II) hydroxide or hydroxide carbonate with hydrogen, respectively (see experimental).

TABLE 2. THE RESULTS

Exp. No.	1_A	1_B	2_A	2_B	3_A	3_B	4_A	4_B	5_A	5_B	6_B	7_A
Amount of liquid products, g	1.68	1.07	1.36	0.90	0.68	0.17	0.58	0.14	0.85	0.08	0.20	2.10
Conversion, %*	4.36	2.75	3.50	2.31	1.76	0.44	1.49	0.36	2.20	0.21	0.52	5.68
Composition of liquid products, %**												
Acetone	29.9	11.0	60.0	11.0	41.0	37.9	62.2	26.0	50.8	45.7	24.3	50.6
Acetaldehyde	5.9	2.6	12.3	3.1	21.0	5.9	10.0	6.9	21.7	1.3	0.3	16.7
dl-2-Butanol	3.0	2.8	3.2	4.0	6.6	8.5	6.7	5.0	6.7	11.3	3.7	6.9
2-Methyl-2-propanol	4.5	4.2	2.7	8.4	8.1	15.6	4.8	8.2	6.4	13.9	9.3	2.0
2-Methyl-2-butanol	0.3	0	0.2	0	0.6	0	0.5	0	0.7	0	2.2	0.6
Isobutyl methyl ketone	0.3	0.7	0.2	0.2	1.6	1.9	1.8	0.9	1.9	4.6	0.6	0
Methyl vinyl ketone	9.6	1.0	0.6	0.8	8.9	8.2	1.2	0	2.2	2.6	1.2	2.8
Hydrocarbons***	43.9	77.7	17.0	72.5	1.4	21.6	8.0	53.0	1.7	17.9	53.0	13.9
dl-2-Pentanol	0.4	0	0.5	0	0.9	0	0.8	0	1.2	0	0	1.2
The others	2.2	0	3.3	0	9.9	0.4	4.0	0	6.7	2.7	5.4	5.3
Gaseous products collected:												
Volume, *l*	2.2	0.5	2.5	1.1	2.5	0.8	1.6	0.5	2.4	0.5	—	—
Components; Methane, Ethylene, Ethane, Acetylene, Propane, Propylene, C_4-Hydrocarbons, Carbon monoxide, Carbon dioxide and Hydrogen.												

* The conversion efficiency was given by (grams of reaction product per grams of 2-propanol used) × 100.

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

*** Hydrocarbons contain 2-methylbutane, 2,3-dimethylbutane, *n*-hexane, 1-hexene, *etc.*

system respectively.

In general, the reaction rate was too low under a reflux system to discuss chemismus.

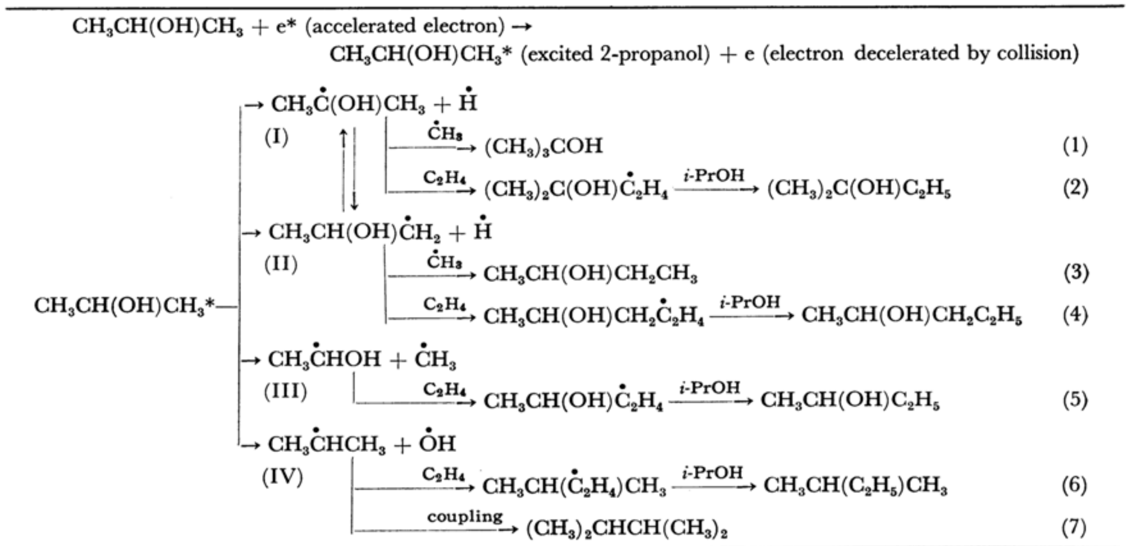
When Siemen's Tube Was Used (Exp. Nos. 6_B and 7_A). The main liquid products formed in the decomposition of 2-propanol at 85°C were acetone, acetaldehyde, *dl*-2-butanol, 2-methyl-2-propanol, and 2,3-dimethylbutane. A small amount of 2-methyl-2-butanol was also formed.

The percentage compositions of compounds shown in Table 2 are the average of three experiments; the fluctuations in the yields of these compounds were less than 1%.

The main gaseous products which were formed in this reaction were methane, ethane, ethylene, acetylene, C_3 and C_4-hydrocarbons, carbon monoxide, carbon dioxide, and hydrogen.

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

Table 3. The assumed radicals and reaction scheme



$$CH_3CH(OH)CH_3 + e^* \text{ (accelerated electron)} \rightarrow CH_3CH(OH)CH_3^* \text{ (excited 2-propanol)} + e \text{ (electron decelerated by collision)}$$

$$CH_3CH(OH)CH_3^* \rightarrow CH_3\dot{C}(OH)CH_3 + \dot{H} \quad \text{(I)}$$

$$\text{(I)} \xrightarrow{\dot{C}H_3} (CH_3)_3COH \qquad (1)$$

$$\text{(I)} \xrightarrow{C_2H_4} (CH_3)_2C(OH)\dot{C}_2H_4 \xrightarrow{i\text{-PrOH}} (CH_3)_2C(OH)C_2H_5 \qquad (2)$$

$$\text{(I)} \rightleftarrows \text{(II)}$$

$$CH_3CH(OH)CH_3^* \rightarrow CH_3CH(OH)\dot{C}H_2 + \dot{H} \quad \text{(II)}$$

$$\text{(II)} \xrightarrow{\dot{C}H_3} CH_3CH(OH)CH_2CH_3 \qquad (3)$$

$$\text{(II)} \xrightarrow{C_2H_4} CH_3CH(OH)CH_2\dot{C}_2H_4 \xrightarrow{i\text{-PrOH}} CH_3CH(OH)CH_2C_2H_5 \qquad (4)$$

$$CH_3CH(OH)CH_3^* \rightarrow CH_3\dot{C}HOH + \dot{C}H_3 \quad \text{(III)}$$

$$\text{(III)} \xrightarrow{C_2H_4} CH_3CH(OH)\dot{C}_2H_4 \xrightarrow{i\text{-PrOH}} CH_3CH(OH)C_2H_5 \qquad (5)$$

$$CH_3CH(OH)CH_3^* \rightarrow CH_3\dot{C}HCH_3 + \dot{O}H \quad \text{(IV)}$$

$$\text{(IV)} \xrightarrow{C_2H_4} CH_3CH(\dot{C}_2H_4)CH_3 \xrightarrow{i\text{-PrOH}} CH_3CH(C_2H_5)CH_3 \qquad (6)$$

$$\text{(IV)} \xrightarrow{\text{coupling}} (CH_3)_2CHCH(CH_3)_2 \qquad (7)$$

molecules,[*3] as has been reported by many workers.[7] The radicals assumed to be formed from 2-propanol under the silent discharge, and a part of the postulated reaction scheme, are shown in Table 3. The methyl radical can be thought to be formed not only in the formation process of the Radical III in Table 3, but also in the secondary reaction, since more methane[*4] than acetaldehyde was produced in every run.

It can be thought that *dl*-2-butanol is formed by two processes: the combination of a methyl radical with a 2-hydroxypropyl radical (Reaction 3), and the addition of a 1-hydroxyethyl radical to the ethylene formed during the reaction (Reaction 5). Although the process of reaction (5) has been proposed in radiolysis,[3] reaction (3) is thought to be the main process for formation of *dl*-2-butanol in the present study, since the yields of C_2-hydrocarbons, including ethylene, are very low.

It has been reported by Bach[8] that the processes induced by the discharge reaction are similar to those induced by radiolysis. However, when present study (Exp. No. 6_B; at 15—32°C) is compared with the study of the radiolysis of liquid 2-propanol,[*5] it is found that the glycols which were produced in the radiolysis were not formed by the discharge.

Much acetone and acetaldehyde were obtained in this reaction. This is similar to the case in the radiolysis of 2-propanol.[3] The dehydrogenation of 2-propanol to give acetone in radiolysis or photolysis has been postulated to occur through the 1-hydroxyisopropyl radical by Atkinson and Di,[9] or through the transfer of a pair of hydrogen atoms from 2-propanol by Raphael *et al.*[10] or McDonell.[*5] In our reaction, the latter seems to be the main process (but not necessarily the only one) for forming acetone, because, were acetone formed by a process such as has been proposed by Atkinson and Di, some pinacols would be produced at the same time by the great quantity of the 1-hydroxyisopropyl radical formed.

Finally, the liquid hydrocarbons seem to be formed

[*3] Devins and Burton found, in the decomposition of ammonia under a silent discharge, that the contribution of ionized molecules was very low; J. C. Devins and M. Burton, *J. Am. Chem. Soc.*, **76**, 2618 (1954).

7) E. G. Linder and A. P. Davis, *J. Phys. Chem.*, **35**, 3649 (1931); S. C. Lind and G. R. Schultze, *ibid.*, **42**, 547 (1938); H. Fujimoto, This Bulletin, **13**, 281 (1938); H. Wiener and M. Burton, *J. Am. Chem. Soc.*, **75**, 5815 (1953); E. Inoue, *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **23**, 574 (1955); S. Takahashi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **79**, 132 (1958).

[*4] The data on the yield of methane is not presented because of the inaccurate data on hydrogen.

8) N. Bach, *Chem. Eng. Progress*, **51**, 478 (1955).

[*5] McDonell and Newton have been reported that the *G*-values of the products formed in the radiolysis of liquid 2-propanol were as follows: H_2 (2.71), C_1—C_4-hydrocarbons (1.76), total carbonyl (2.96), *vic*-glycols (0.39); W. R. McDonell and A. S. Newton, *J. Am. Chem. Soc.*, **76**, 4651 (1954). Spinks and Woods have discussed how the products of the radiolysis of liquid methanol are very similar to those of the radiolysis of methanol vapor, and so are those of the radiolysis of ethanol. Therefore, the products of the radiolysis of 2-propanol vapor are thought to be similar to those of the radiolysis of the liquid 2-propanol; J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, New York (1964).

9) B. Atkinson and M. Di, *Trans. Faraday Soc.*, **54**, 1331 (1958).

10) R. A. Raphael, E. C. Taylor and H. Wynberg, "Advances in Organic Chemistry," Vol. II, Interscience Publishers, New York (1960), p. 355.

through the isopropyl radical, which may be derived from the excited 2-propanol.

Whan a Special Tube Filled with Copper or Its Salts Was Used. It has been discussed in detail by Semenov[11] how, in photolysis, the reaction products are greatly affected by the nature of the substances forming the wall, as well as by the size of the vessel. However, Inoue[12] found, in a discharge reaction, that the size of the vessel had no influence on the reaction rate. In order to check the wall effects on the decomposition of 2-propanol, the reaction was carried out in a tube packed with copper or its salts (all runs except Nos. 6_B and 7_A in Tables 1 and 2).

Comparing the Glassy Wall with a Wall of Copper or Its Salts. The product pattern was somewhat simplified by changing the glassy wall to a copper(II) hydroxide wall. For example, the gas chromatogram showed seventeen peaks for the products from the 7_A run, but only ten peaks for the 1_A run (PEG-6000, 100°C, He). Thus, the former contains more kinds of hydrocarbons and unidentified, high-boiling products than 1_A.

A similar product pattern was obtained in the presence of the other packing materials, too, except in the case of metallic copper. When the reaction was carried out in a tube with a metallic copper wall (Exp. No. 5_A), the percentages of all the liquid products except hydrocarbons and acetaldehyde were almost the same as with 7_A (using glass walls).

The reaction rate and the amounts of 2-methyl-2-butanol, *dl*-2-pentanol, and all the carbonyl compounds except methyl vinyl ketone were greatest when the glassy-wall tube was used.

Effects of Packing Substances. When the two reduced coppers, 1 and 2 (Exp. Nos. 2_A and 4_A respectively), were used as packing, as compared with the original copper salts (Exp. Nos. 1_A and 3_A), the following differences were noticed in the liquid products: (1) the acetone yield increased remarkably; (2) the yields of 2-methyl-2-propanol and methyl vinyl ketone decreased; and (3) the relative yields of *dl*-2-butanol, 2-methyl-2-butanol, and *dl*-2-pentanol were almost the same, regardless of the reduction treatment.

The reason why the 2-propanol excited by the discharge changes almost entirely into acetone in the presence of the reduced coppers is considered to be as follows: Metallic copper and reduced copper are effective catalysts for the dehydrogenation of alcohols.[13] Although these coppers behave excellently as catalysts, usually at a high temperature, Taylor[14] showed that the irradiation of radioactive rays makes a solid catalyst active, even at a low temperature, by destroying the catalyst poison, forming a positive hole on the surface, trapping electrons, *etc.* Similar effects might be brought about by the silent discharge.

2-Methyl-2-propanol, hydrocarbons, and methyl vinyl ketone were obtained in the highest yields when copper(II) hydroxide was used as packing (Exp. No. 1_A). This packing material aids in forming hydrocarbons especially. This fact implies that the C–O-bond breaking in 2-propanol occurs rather preferably in the presence of this material.

On the other hand, relatively much methyl vinyl ketone was produced in the presence of copper salts. This product may be formed by the combination of a vinyl radical with an acetyl radical. The acetyl radical can be thought to be formed by a secondary reaction of the acetone or acetaldehyde produced, since the photolysis[15] and the radiolysis[16] of acetone and acetaldehyde have been known to produce the acetyl radicals. The vinyl radical can be formed by the elimination of a hydrogen atom from the ethylene produced under a silent discharge, as has been suggested by Tsutsumi[17] and by Thomas *et al.*[18] The yields of ethylene, acetylene, 1-butene, and 1,3-butadiene in gaseous products were highest in the presence of copper salts. Therefore, the vinyl radical seems to be increased in those cases. For this reason, the methyl vinyl ketone may be obtained in the highest yield in the presence of copper salts.

The main conclusions to be drawn from these results are as follows: (1) Despite the different kinds of discharge tubes, the liquid products consisted of similar components, but the compositions of the products depend on the kind of tube. (2) The 2-hydroxypropyl radical was regarded as an important intermediate in the reaction. (3) The only radical addition product was the one-to-one adduct. (4) On the wall of copper(II) hydroxide, C–O-bond breaking in the 2-propanol occurred rather preferably upon the discharge. (5) Copper(II) hydroxide and hydroxide carbonate might give more of the vinyl radical than other materials. (6) Generally speaking, the selectivity was a little higher in the presence of packing than in its absence.

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[11] N. N. Semenov, "On Some Problems of Chemical Kinetics and Reactivity," USSR Academy of Sciences Printing House, Moscow (1958).

[12] E. Inoue, *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **23**, 76 (1955).

[13] P. Sabatier and J. B. Senderens, *Compt. Rend.*, **136**, 738, 921, 983 (1903).

[14] E. H. Taylor, *Nucleonics*, **20**, (Jan.), 53 (1962).

[15] W. A. Noyes, Jr. and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

[16] P. Ausloos and J. F. Paulson, *J. Am. Chem. Soc.*, **80**, 5117 (1958).

[17] S. Tsutsumi, *Chem. Ind.*, **16**, 623 (1965).

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