[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VIII. A Comparison of the Thermal and Electrical Decomposition of Organic Compounds into Free Radicals

BY F. O. RICE AND FRED R. WHALEY[1]

In a previous paper of this series it was shown that when organic compounds are heated[2] at low pressures they decompose into free radicals, which can be detected by the Paneth[3] effect on metallic mirrors; to supplement these experiments it seemed desirable to see whether organic compounds could be decomposed into free radicals by electrical means instead of by heat. In this paper we shall give an account of some experiments with the fragments produced in a discharge tube, and compare them with similar experiments in which the same compounds were decomposed thermally. This is only a preliminary account since it was necessary to interrupt the work before it could be brought to completion.

Thermal Decomposition

The experimental results on the thermal decomposition of organic compounds are shown in Table I; the technique of this method has already been published.[2] The most striking behavior was shown by ethylene[4] since even very thin antimony mirrors were not affected after ethylene[5] had passed over them for fifteen minutes from a furnace heated to about 1000°. This experiment is interesting in connection with the suggestion[6] that divalent radicals such as $—CH_2—CH_2—$ may be formed by the action of heat on unsaturated organic compounds and may play a part in the decomposition mechanism. If the divalent radical $—CH_2—CH_2—$ is formed at all, it either must have an exceedingly short life or it does not react with antimony mirrors. Furthermore, this observation provides evidence against the possibility that mirror removal may be caused by "hot molecules" which still have energy much above the average when they collide with the cold metallic mirror.[7]

TABLE I

THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS INTO FREE RADICALS

F = removal of a standard mirror in less than one minute; S = removal in one to fifteen minutes; X = mirror not removed after fifteen minutes. We have confirmed results previously published[2] for ethane, propane, butane and trimethylamine.

Temperature, 850–950°. Pressure, 0.2–2.0 mm.

Organic compound	Pb	Sb
Ethane	V.s.	S
Propane	F	F
Butane	F	F
Isobutane	F	F
Heptane	F	F
Gasoline	F	F
Diethyl ether	F	F
Propionic aldehyde	V.s.	S
Ethylene	X	X
Propylene	S	S
Acetic acid	X	S
Ethyl acetate	V.s.	S
Ethyl propionate	F	F
Ethyl maleate	X	S
n-Butyl alcohol	F	F
Trimethylamine	F	F

Electrical Decomposition

The apparatus used for investigating the electrical decomposition of organic compounds is very similar to that described in a previous publication [Ref. 2, Fig. 3] for studying thermal decompositions. The furnace is replaced by a short section of a discharge tube formed by fitting the furnace tube with two side arms 3–4 cm. apart. The side arms contained electrodes of sheet aluminum connected with a 500-watt transformer furnishing 10,000 volts. The whole apparatus was of Pyrex glass.

Using this apparatus we found that mirrors of antimony and lead were removed by the fragments formed in the decomposition of various compounds. The results are summarized in Table II.

We also obtained the curious result, which we cannot yet explain, that the fragments formed in these electrical decompositions do not remove zinc

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(1) Graffin Fellow, 1931.

(2) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932); see also Rice and Dooley, *ibid.*, **55**, 4245 (1933); Rice and Johnston, *ibid.*, **56**, 214 (1934).

(3) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(4) Paneth and Hofeditz, *ibid.*, **62**, 1343 (1929), report that ethylene passed through a hot tube will remove antimony mirrors slowly leaving a carbon deposit in the tube. They note, however, that the removal may be due to impurities in their sample of ethylene.

(5) A very pure sample of commercial ethylene, which we distilled through a vacuum jacketed still, was used in this experiment.

(6) See Hurd, *Ind. Eng. Chem.*, **26**, 50 (1934).

(7) See Burk, *J. Phys. Chem.*, **35**, 2446 (1931).

TABLE II

THE EFFECT OF FRAGMENTS FORMED IN A DISCHARGE TUBE

F = removal in less than one minute; S = removal in one to fifteen minutes; X = not removed after fifteen minutes.

	Sb	Pb
n-Butane	F	
n-Heptane	F	
Ethylene	F	S
Methyl alcohol	F	F
Ethyl alcohol	F	F
Acetaldehyde	F	F
Acetic acid	F	F
Acetone	F	F

or cadmium mirrors. There is, of course, the possibility that the active fragments consist only of atomic hydrogen, which would explain the non-removal of zinc and cadmium mirrors.[8] However, as we shall show later, we were able to identify methyl groups among the decomposition products in some of the experiments and, furthermore, it now seems to be definitely established that atomic hydrogen does not remove lead mirrors[9] whereas in our experiments the latter were promptly attacked.

We next made some measurements of the life of the active agent produced in the discharge tube, following the method of Paneth and Hofeditz.

The concentration of the fragments at the different points was assumed to be proportional to the speed with which standard mirrors were removed at that point. The pressure of vapor at the mirrors was measured, as was also the quantity of material passing through the apparatus, so that we could determine the time taken for the fragments to pass from the discharge tube to the standard mirror. Table III contains the results of two experiments for acetone and butane. We performed four experiments using acetone and one experiment using butane. The constants calculated according to a first order equation showed considerable drift and gave a half life between 0.65 and 1.3 × 10^{-3} sec.; the half life obtained for the fragments from butane was 2.1 × 10^{-3} sec. These values may be compared with the value 6 × 10^{-3} sec. obtained by Paneth[4] for methyl groups and 1–2 × 10^{-3} sec. obtained by Rice, Johnston and Evering.[2]

TABLE III

DISCHARGE TUBE EXPERIMENTS RATE OF DISAPPEARANCE OF FRAGMENTS FROM BUTANE AND ACETONE

Acetone d_m, cm.	Acetone $\Delta t \times 10^4$, sec.	Acetone t_m, sec.	Butane d_m, cm.	Butane $\Delta t \times 10^4$, sec.	Butane t_m, sec.
5.5	15.6	19	8.5	55.3	30
9.5	27.0	52	11.5	75.0	54
12.0	34.2	123	12.0	78.0	71

d_m, the distance from the center of the discharge tube to the standard mirror; Δt, time taken to travel from the discharge tube to the mirror; t_m, time required to remove mirror. Cross section of tube 0.8 cm. Pressure of butane at discharge tube 0.15 mm.; fall in pressure, 0.001 mm. per cm. length. Pressure of acetone at mirror 0.073 mm.; fall in pressure of acetone 0.004 mm. per cm. length.

Identification

We further attempted to obtain positive identification of the fragments by combining them with mercury to form mercury dialkyls, which could then be identified as the corresponding alkyl mercuric bromides. The apparatus used is very similar to that described in a previous publication [Ref. 2, Fig. 3] except that a discharge tube replaces the furnace. Any alkyl radicals formed would be expected to combine with the cold mercury on the walls to form mercury dialkyls, which would then pass into the liquid air trap. The latter can be identified through their alkyl mercuric bromides.

In our first experiment we passed 25 cc. of acetone through the discharge tube in one hour. After the addition of an excess of alcoholic mercuric bromide to the contents of the liquid air trap and evaporation and sublimation of the product at 70° we obtained less than 0.1 g. of a white substance which partly decomposed at 130–135° leaving a black residue in the tube. A second sublimation at 40° yielded a small quantity of a white substance which proved to be methyl mercuric bromide (its m. p. of 160° was unchanged on mixing with a pure sample made by the Grignard reaction).

The removal of antimony mirrors by fragments produced from ethylene in the discharge tube warranted an attempt to see whether alkyl radicals were formed. Consequently 13 cc. of ethylene was passed through the discharge tube in twenty-five minutes and the products were caught in the liquid air trap. An excess of alcoholic mercuric bromide was added as before, but after evaporation we could not detect any organomercuric compound in the residue.

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(8) Paneth, *Ber.*, **58**, 1138 (1925). In this connection it may be noted that Willey, *Trans. Faraday Soc.*, **30**, 230 (1933), has found zinc dimethyl in the electrical decomposition of methane when a zinc cathode was used.

(9) Pearson, Robinson and Stoddart, *Proc. Roy. Soc.* (London), **A142**, 275 (1933).

A third experiment was performed using methyl alcohol; a very small quantity of some substance which decomposed at 133° leaving a black residue was sublimed from the residue in the liquid air trap after reaction with mercuric bromide; there was no evidence of methyl groups.

In our fourth experiment 25 cc. of butane was passed through the discharge tube in one hundred and five minutes. A small quantity of some substance which melted a little below 144° was obtained, but it was contaminated by some other product which also decomposed at about this temperature. This behavior suggests the presence of alkyl mercuric bromides.

We decided to examine further the identity of the products obtained in these runs by taking x-ray powder photographs and comparing these with photographs of the known alkyl mercuric bromides both in the pure state and sublimed together; we also photographed at the same time the products obtained in the thermal decomposition of butane. The samples were packed into collodion tubes of about 0.5 mm. diameter and 5–10 mm. long and inserted in an x-ray camera; the camera was installed at one window of an x-ray tube which gave principally Cu K_α radiation, for which $\lambda = 1.54 \times 10^{-8}$ cm. (a nickel filter was used to remove K_β). The same camera was used for all the pictures taken, and the camera was of such size that the distance, x, between corresponding lines on opposite sides of the undeflected beam, expressed in mm. equalled twice the glancing angle expressed in degrees. The results are shown in Fig. 1, but unfortunately due either to solid solution or compound formation do not give unequivocal evidence as to the composition of the products. The first six photographs are of the pure compounds or synthetic mixtures. The seventh photograph is of the alkyl mercuric bromides obtained by treating the mercury dialkyls formed in the thermal decomposition of butane at about 850° with alcoholic mercuric bromide. This appears to indicate a mixture of the methyl and ethyl derivatives but a repetition of the experiment at about 950° (photographs 8 and 9) indicates that only the methyl derivative is present. The product obtained from the acetone discharge indicates mainly the methyl derivative whereas the product from the butane discharge (contaminated with mercuric bromide) could not be identified. There was no evidence of propyl groups in any of the products examined.

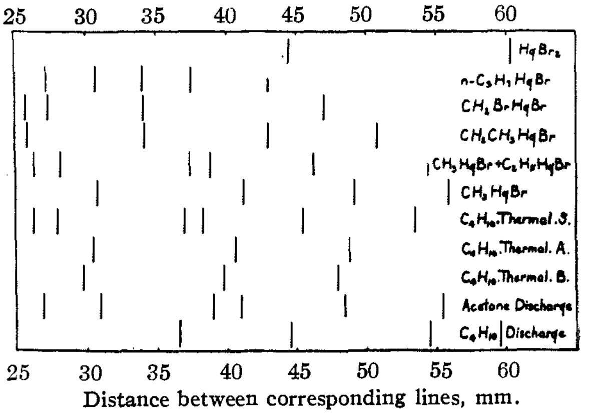

Fig. 1.—x-Ray spectra of organo compounds of mercury. C_4H_{10}: Thermal S products obtained from thermal decomposition of butane at about 850°. C_4H_{10}: Thermal A and B, products obtained from thermal decomposition of butane at about 950°, first and second fractions, respectively. The last two spectra are those of the products of the electrical decomposition of acetone and butane, respectively. The spectra in the last five cases are of the alkyl mercuric bromides formed by passing the mercury alkyls first produced into alcoholic mercuric bromide.

Summary

1. A number of organic compounds when heated in the range 800–1000° at low pressures have been shown to decompose into fragments which remove lead and antimony mirrors. Ethylene is exceptional in that it gives no active fragments; from this we may conclude that if the divalent radical —CH_2—CH_2— is formed at all, it does not attack either lead or antimony mirrors or it has an exceedingly short life.

2. A number of organic compounds have been passed through a discharge tube and shown to form fragments which remove lead and antimony mirrors and have a half life in the range 0.7–2.1 $\times 10^{-3}$ sec. These fragments do not seem to react with zinc or cadmium mirrors.

3. x-Ray powder photographs were taken of organic mercuric bromides obtained in some of these experiments. The results gave further confirmation that methyl groups are formed in the decomposition of acetone in a discharge tube. The results for butane were not conclusive but indicate that methyl radicals are formed when it is decomposed thermally. There was no indication of propyl groups in any of the decomposition products examined.

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