[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Free Radicals in the Pyrolysis of Acetaldehyde

BY MILTON BURTON, JOHN E. RICCI AND THOMAS W. DAVIS

Leighton and Mortensen[1] have described experiments in which they detected the formation of free alkyl radicals by the transport of radioactivity (due to Ra-D) from a Paneth radio-lead mirror over which the radicals were passed.[2] We have modified their method in regard to the collection of the transported Ra-D and have been successful in this way in establishing the formation of free radicals in the pyrolysis of acetaldehyde at 500°.

Experimental

The apparatus used in this investigation was essentially as shown in Fig. 1.

Eastman Kodak Co. acetaldehyde was distilled into reservoir A immersed in dry-ice from a reservoir cooled with ice and subsequently freed from air by repeated alternate warming and evacuation at dry-ice temperatures. In this way the extensive polymerization caused by freezing in liquid air[3] was largely avoided. Of two samples so prepared, one, used in runs 17 to 25, had a v. p. of ~335.6 mm., and the other, used in runs 26 to 34, had a v. p. of ~334.6 mm. at 0°. Comparison of these values with that of 337 mm. given by Emeleus[4] would indicate that the presence of the polymer, which could be readily discerned as acetaldehyde was removed, decreased the vapor pressure.

Pellets of natural radio-lead (Pb) prepared from spent radon tubes[5] in a manner already described[6] were introduced into the system (beyond the graded seal G) at a fracture at C which was thereafter sealed. The section of tubing extending to the right of the furnace had an internal diameter of ~5 mm. Heavy mirrors, ~5–6 mm. long in runs 16 to 25 and ~1 cm. long in runs 26 to 34 were deposited at B at a distance ≤ 4 cm. from the end of an electrically heated quartz furnace Q. Because of the presence of radioactive materials it was necessary to modify the usual methods of deposition.[2] Before each deposition any remnant of old mirror was removed by external heating with a gas flame while a stream of acetaldehyde vapor passed through the tube via stopcocks 2, 3 and 4. A fresh mirror was then driven ahead of a gas flame toward the furnace in the usual way and deposited instead of the old. This was removed in the manner just described and a new mirror was deposited for the run. In order to remove the last trace of any volatile radioactive compound the system was now pumped out for several hours before the actual commencement of the run. It is known that delay in the use of lead mirrors decreases their sensitivity to free radicals. It is our opinion that, because of the delay, the mirrors so prepared had both variable and limited active surface. As a result, the figures we list in Table I can be compared only qualitatively with one another. Consequently any temperature coefficients derived from them would be without significance.

During runs, with the exception of the blanks 17, 19 and 22, the mirror was heated externally by steam.[7]

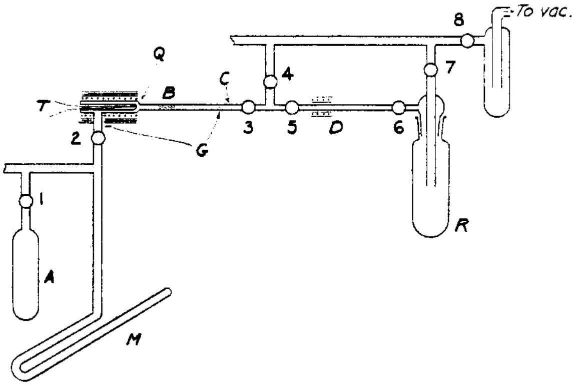

Fig. 1.—Set-up of apparatus.

The temperature of the furnace Q (which was ~10 cm. in length and ~1.2 cm. in internal diameter, and whose well was ~0.8 cm. in outer diameter) was measured with a thermocouple T extending to the tip of the well. Observations, not here recorded, showed a temperature variation along the well with a maximum somewhat higher than at the tip. In the experiments at higher temperature (*i. e.*, ~650°) the maximum was ~50° greater than the observed value while in the lower temperature experiments it was probably no more than 40° above the observed.

During runs, the pressure of acetaldehyde vapor at the stopcock 2, measured on the sloping manometer M, was ~4 mm. The lead tetramethyl presumably formed at the mirror (together with polonium alkyls) was carried by the vapor through stopcocks 3 and 5 to a section of glass tubing heated by the movable heater D to a temperature of 400–500°. Since $Pb(CH_3)_4$ is unstable at such temperatures,[2] free Pb deposited in the tubing near the ends of the "cracking furnace." At the end of a run, stopcocks 1, 3, 5 and 6 were closed, stopcock 4 was opened and the segment of tubing containing the deposited lead was cut out. The lead was dissolved in hot dilute nitric acid and the solution was evaporated to dryness. The radioactivity of the lead nitrate so produced was determined by noting its effect on the rate of discharge of a Lind electroscope into which it was introduced. The net activity (expressed in reciprocal minutes) was in each case corrected for the apparent activity of the empty dish.

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[1] P. A. Leighton and R. A. Mortensen, THIS JOURNAL, **58**, 448 (1936).

[2] *Cf.* F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

[3] *Cf.* M. W. Travers, *Trans. Faraday Soc.*, **32**, 246 (1936).

[4] H. J. Emeleus, *J. Chem. Soc.*, 1733 (1929).

[5] We are indebted to Dr. Otto Glasser of the Cleveland Clinic, Cleveland, O., and to Dr. Roscoe W. Teahan of the Jeanes Hospital, Philadelphia, Pa., for the gift of these tubes.

[6] J. E. Ricci and M. Burton, THIS JOURNAL, **60**, 727 (1938).

[7] *Cf.* T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, 1151 (1935).

In order to check the possibility that a substantial amount of Pb might actually be passing the "cracking furnace" D without deposition, a second such heater was installed to the right of the first and both heated segments of tubing were examined for radioactivity after the runs. In every positive case tested the activity of the right-hand sample was $<1/4$ that of the left-hand sample.

The results of the experiments are summarized in Table I. Each of the runs reported lasted approximately forty-eight minutes. All the pertinent data of the investigation are included in the table; the runs prior to those listed were used in developing the technique of the method. After run 34 the whole system became so seriously contaminated with radio-lead, when the latter was through error introduced into the furnace, that the work had to be abandoned.

TABLE I

TRANSPORT OF RADIO-LEAD IN THE PYROLYSIS OF ACETALDEHYDE

Run	CH_3CHO press., mm.	Furnace temp., °C.	Distance of mirror from furnace, cm.	Net activity, min.$^{-1}$
17[a]	4.0	Room	3.5–4	0.0038
18	4.0	550–560	3.5–4	.38
19[a]	4.0	Room	3.5–4	.027
20	4.0	550–560	3.5–4	.060
21	4.0	550–560	3.5–4	.23
22[a]	4.0	Room	3.5–4	.0018
23	4.0	650	3.5–4	.18
24	0	660	3.5–4	.0054
25	4.0	650–660	3.5–4	.22
26	0	660	3.5–4	.044
27	0	650	3.5–4	.013
28	4.1	460–465	4	.11
29	4.0	460	4	.16
30	4.2	663	2.8	.70
31	4.2	660–670	3.5	.28
32	4.0	352	3	.017
33	0	660	3	.026
34	4.0	375	2.7	.007

[a] The Pb* mirror was cold in experiments 17, 19 and 22.

Discussion

Runs 17, 19 and 22 were blanks in which both furnace and mirror were at room temperature with acetaldehyde flowing through the system. Runs 24, 26, 27 and 33 were blanks in which the furnace and mirror were both heated (the latter with steam) and no acetaldehyde was flowing. These experiments clearly showed that a negligible quantity of radio-lead was transported either by free flow of vapor or by possible volatilization of Pb* at steam temperature. In runs 32 and 34, with the furnace heated to 352 and 375°, respectively, a negligible transfer occurred, thus demonstrating that only acetaldehyde heated to a sufficiently high temperature, that is, the decomposed substance, was effective in transporting Pb*.

The low net activity in run 20 is perhaps to be attributed to a chance preparation of an insensitive mirror. The average activity, in min.$^{-1}$, observed for the other actual tests (18, 21, 23, 25, 28, 29, 30, 31) is 0.28, with limits 0.11 to 0.70. The average activity for the blank experiments (17, 19, 22, 24, 26, 27, 33) is 0.016, with limits 0.0018 to 0.044. In our opinion the difference is real, and on this basis the results of experiments 32 and 34 can be called negative. The lowest temperature (of the tip of the thermocouple) at which transfer was clearly established was 460°, corresponding to a maximum temperature in the furnace of $\sim$500°.

The lowest temperature at which the pyrolysis of acetaldehyde appears to have been studied is 430°[8] but the more detailed work has been done at slightly higher temperatures ($\sim$475°).[9] Staveley and Hinshelwood[10] have stated that "the photochemical production of free radicals, which might in any case be expected, from what we know of other catalysts, to have a catalytic action on the decomposition of acetaldehyde, does not prove their occurrence in the thermal reaction." Neither, it may be said, does the decomposition induced[11] by azomethane. The lowest temperature at which the actual detection of free radicals has been reported hitherto in the pyrolysis of acetaldehyde is 743°.[12] The results here presented, however, seem clearly to demonstrate the existence of free radicals in the products of the pyrolysis at $\sim$500° and it seems probable, therefore, that they exist in the products of the pyrolysis at the lowest temperatures studied, as indicated by the Rice–Herzfeld mechanism.[13]

The data of Table I are sufficient for decision as to the existence or non-existence of free radicals under a particular set of conditions but are not satisfactory for quantitative estimation of numbers or of relative numbers of free radicals formed. Work of a more quantitative nature is being continued with artificial radio-antimony, with which substance complications caused by the existence

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(8) C. N. Hinshelwood and W. K. Hutchison, *Proc. Roy. Soc.* (London), **A111**, 380 (1926).

(9) *Cf.* M. Letort, *Compt. rend.*, **199**, 351 (1934); *ibid.*, **200**, 312 (1935).

(10) L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 812 (1936).

(11) D. V. Sickman and A. O. Allen, THIS JOURNAL, **56**, 1251 (1934).

(12) F. O. Rice and W. R. Johnston, *ibid.*, **56**, 214 (1934).

(13) F. O. Rice and K. F. Herzfeld, *ibid.*, **56**, 284 (1934); *cf.* H. A. Taylor and M. Burton, *J. Chem. Phys.*, **7**, 414 (1939); T. W. Davis and M. Burton, *ibid.*, **7**, 1075 (1939).

of radioactive recoil particles, as from the radiodecomposition of Pb*, can be avoided.

Summary

The method of Leighton and Mortensen employing natural radio-lead in Paneth mirrors has been modified and used for the detection of low concentrations of free radicals.

In this way the existence of free radicals in the pyrolysis of acetaldehyde at 500° has been detected.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. VII. The Vapor Phase Fluorination of Ethyl Chloride

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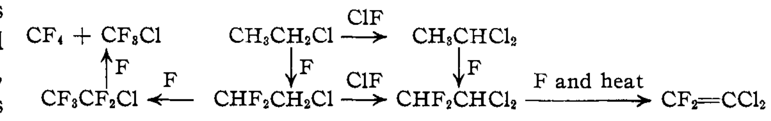
In the third paper of this series,[1] we discussed the vapor phase fluorination of hexachloroethane over copper gauze, which resulted in the substitution of chlorine by fluorine, and yielded *sym*-difluorotetrachloroethane. Since then we have developed an improved technique for the fluorination of organic gases,[2] and this paper deals with the interesting results obtained by applying it to ethyl chloride. Fluorination and chlorination took place simultaneously during the reaction.

Results and Discussion

The ethyl chloride was fluorinated smoothly in a metal apparatus, over copper gauze, under conditions described fully before.[2] The products were condensed by liquid air, transferred to a Booth–Podbielniak low temperature fractionating unit, separated, rectified and analyzed. There were formed carbon tetrafluoride, trifluorochloromethane, CF_3Cl, b. p. −80° (−80°)[3]; pentafluorochloroethane, CF_3CF_2Cl, b. p. −38° (−38°)[4] m. p. −106°; 1,1,2,2-difluorodichloroethylene, $CF_2{=}CCl_2$, b. p. 0° (15°?),[4] m. p. −116°; 1,1,2-difluorochloroethane, CHF_2CH_2Cl, b. p. 35° (35°)[5]; and other products. The observed molecular weights agreed well with the calculated values. The last of these compounds was washed with dilute alkali, dried and distilled in the ordinary way, and the ethylene derivative was passed through a 5% sodium hydroxide solution before analysis. The difluoro- and pentafluoroethyl chloride, as well as the difluorodichloroethylene, have not been obtained before by direct fluorination.

Henne and Renoll[5] gave the boiling point of $CF_2{=}CCl_2$ as 15°, whereas we have found it to be 0°. However, they did not report any molecular weight or analysis, while the values given in Table II leave no doubt as to the composition of the sample which we have examined. The only possible isomer of this compound, $CFCl{=}CFCl$, boils at 20.9° according to Booth and collaborators.[6]

In addition to the compounds which were isolated, several others were produced in lesser quantities. A small fraction boiling near 60° was observed repeatedly, and when a larger portion containing this material was distilled at reduced pressure, two small samples were obtained, one of which had a molecular weight of 135, and the other of 98. Now the compound CHF_2CHCl_2 (mol. wt. 135) boils at 60°,[7] and ethylidene chloride CH_3CHCl_2 (mol. wt. 99), distils at 57°. It therefore seemed likely that the two last-named compounds were formed during the reaction. Granting this, a partial mechanism for the fluorination of ethyl chloride may be represented tentatively as



$$\begin{tikzcd}
CF_4 + CF_3Cl & CH_3CH_2Cl \arrow[r, "ClF"] \arrow[d, "F"] & CH_3CHCl_2 \arrow[d, "F"] & \\
CF_3CF_2Cl \arrow[u, "F"] & CHF_2CH_2Cl \arrow[l, "F"'] \arrow[r, "ClF"] & CHF_2CHCl_2 \arrow[r, "F\ and\ heat"] & CF_2{=}CCl_2
\end{tikzcd}$$

This mechanism involves the substitution of chlorine by fluorine, $RCl + 2F \longrightarrow RF + ClF$, and chlorination by chlorine fluoride, $RH + ClF \longrightarrow RCl + HF$. The reaction $RCl + HF \longrightarrow RF + HCl$ may occur, but this seems doubtful.

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(1) Miller, Calfee and Bigelow, THIS JOURNAL, **59**, 198 (1937).

(2) Calfee and Bigelow, *ibid.*, **59**, 2072 (1937); Calfee, Fukuhara and Bigelow, *ibid.*, **61**, 3552 (1939).

(3) Ruff and Keim, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).

(4) Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

(5) Henne and Renoll, *ibid.*, **58**, 889 (1936).

(6) Booth, Burchfield, Bixby and McKelvey, THIS JOURNAL, **55**, 2231 (1933).

(7) M. Swartz, *Bull. soc. chim.*, **35**, 1557 (1924).