543. *The Pyrolysis of* tert.*-Butyl Formate.*

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The thermal decomposition of *tert.*-butyl formate into *iso*butene and formic acid has been studied in a static system at temperatures between 230° and 300° c. The decomposition is homogeneous and obeys first-order kinetics in its early stages; the rate constant is given by

$$\log_{10} k(\text{sec.}^{-1}) = 11{\cdot}1 - (34{,}600/2{\cdot}303\boldsymbol{R}T)$$

The elimination of formic acid is probably a molecular process, as the addition of *cyclo*hexene has a very small effect on the rate. The rate of this reaction is reasonably related to the rates of similar decompositions.

Determinations of the rate constants of the decompositions of ethyl, *iso*propyl, and *tert.*-butyl chlorides, bromides, and acetates have all been reported in the literature.[1] No measurements have been reported on the decompositions of *tert.*-butyl formate although the ethyl and *iso*propyl derivatives have been investigated. The object of the present study was to fill this gap.

Experimental

Materials.—The *tert.*-butyl formate was specially prepared for use in this investigation by Dr. C. Barkenbus (University of Kentucky) according to his method.[2] The material was thoroughly degassed and stored in solid carbon dioxide. It was found that at temperatures appreciably above room temperature and in the absence of a drying agent the liquid rapidly decomposed, apparently into *iso*butene and formic acid. The *cyclo*hexene, which was also degassed, was freed from peroxides by shaking it with acidic ferrous sulphate solution.

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[1] For full references see Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, and Maccoll and Thomas, *Nature*, 1955, **176**, 392.

[2] Barkenbus, Naff and Rapp, *J. Org. Chem.*, 1954, **19**, 1316.

Apparatus.—The decomposition was studied in a 385-c.c. Pyrex bulb attached to a conventional vacuum system by heated tubing; the total dead space was approximately 13 c.c. The empty bulb had a surface : volume ratio of 0·9 cm.$^{-1}$; when it was packed with fire-polished Pyrex tubing the ratio was 3·0 cm.$^{-1}$. The bulb was contained in a mercury-vapour jacket, whose temperature could be controlled readily by varying the pressure under which the mercury boiled. The temperature of the jacket was determined by reference to standard tables of the vapour pressure of mercury. The reaction was studied by following the change in pressure in the reaction vessel on a mercury manometer.

Procedure.—Runs were started by admitting a suitable quantity of the formate to the reaction vessel from the storage bulb; in some runs *cyclo*hexene was also added. Readings of the pressure in the vessel were then recorded at convenient intervals. Rate constants were determined from first-order plots of the logarithms of the pressure changes against time, based on the assumption that complete reaction corresponded to a doubling of the pressure. The logarithmic plots were strictly linear for the first 70—80% of the reaction at the higher temperatures but thereafter tended to curve slightly. No induction periods were observed.

RESULTS AND DISCUSSION

tert.-Butyl formate was presumed to yield formic acid and *iso*butene as the primary products of the decomposition. This presumption is based upon the known ease with which these products are formed in the liquid in the presence of a trace of acid and upon the analogy with the decompositions of the other formates. It was difficult to check this by analysis, because of the rapidity with which the liquid decomposed. Several experiments were done with a trap system in which the formate and formic acid were condensed in a trap cooled in solid carbon dioxide and the *iso*butene in a trap cooled in liquid oxygen. The *iso*butene was then transferred back into the reaction system and its pressure measured. The percentage decomposition based on the formation of *iso*butene was then calculated. The results of a series of runs at 251° were:

Percentage decomposition by pressure rise	11·4	19·0	30·0	41·0
Percentage decomposition by *iso*butene	7·9	14·4	30·0	39·0

The method of analysis was not very satisfactory, but there appears to be little doubt as to the nature of the decomposition. Runs which were followed for many half-lives never yielded a pressure greater than twice the initial pressure. This is evidence that the formic acid does not decompose at these low temperatures.

The linearity of the logarithmic plots demonstrated the first-order nature of the decomposition which was confirmed by runs with different initial pressures of the formate between 3·8 and 10·3 cm. No systematic trend or variation of the rate constants outside the limit of experimental error was observed.

Fig. 1 is an Arrhenius plot of the rate constants for the thermal decomposition. The best straight line was calculated by the method of least squares giving equal weight to each run: the points shown in the Figure are the mean values obtained at each temperature. The results are best expressed by

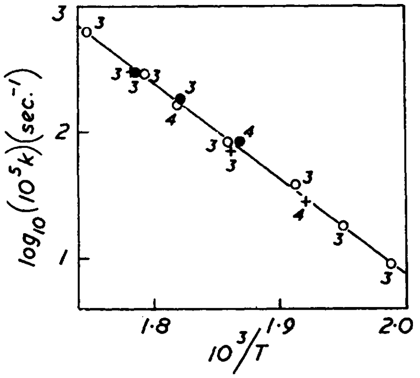
$$\log_{10} k(\text{sec.}^{-1}) = 11{\cdot}1 - [(34{,}600 \pm 900)/2{\cdot}303\boldsymbol{R}T]$$

Two facts showed the decomposition to be homogeneous. First, no conditioning of the reaction vessel was needed before reproducible results were obtained. Second, packing the reaction vessel did not affect the rate constants, as is shown in Fig. 1 where the mean results obtained in the packed vessel are plotted.

The absence of an induction period and the negligible effect of packing the vessel indicate that the decomposition is molecular and does not involve free radicals. This was confirmed by adding *cyclo*hexene to the system; 20—50% of *cyclo*hexene appeared to reduce the rate of decomposition very slightly, but the lowering was of the same order as the experimental scatter. The results obtained with *cyclo*hexene are also shown in Fig. 1.

The activation energy of this decomposition is markedly lower than those for the decomposition[3] of ethyl (44·1 kcal. mole^{-1}) and of *iso*propyl formate (44·0 kcal. mole^{-1}). However, it is often more enlightening to compare the variation of the rate constants of a series of reactions rather than their *A* factors and activation energies. Such a comparison is made for several series of ethyl, *iso*propyl, and *tert.*-butyl esters in Fig. 2. All of these decompositions are thought to be molecular. The rate constants are corrected to 380° and are expressed in terms of the rate constant of the ethyl ester which has been assigned the value unity. In the figure the logarithms of the rate constants are plotted against the logarithms of the rate constants for the decomposition of the ethyl, *iso*propyl, and *tert.*-butyl bromides. The line labelled " hydrides " represents the rate constants for the decompositions of ethyl bromide, *n*-propyl bromide, and *iso*butyl bromide. It is evident that the same factors control the rates of each series of reactions.

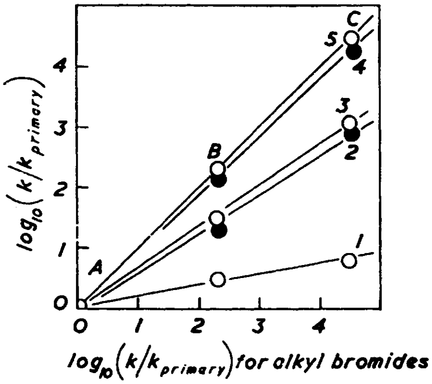
FIG. 1. *Arrhenius plot for the thermal decomposition of* tert.-*butyl formate.*



○ Unpacked vessel. ● Packed vessel. + Unpacked vessel with the addition of *cyclo*hexene.

The figures by the circles indicate the number of runs averaged to obtain each point.

FIG. 2. *The relation between the rates of the molecular decompositions of various ethyl,* iso*propyl, and* tert.-*butyl derivatives.*



A, Ethyl. *B*, *iso*Propyl. *C*, *tert.*-Butyl.
1, Hydrides. 2, Formates. 3, Acetates.
4, Chlorides. 5, Bromides.

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[3] Blades, *Canad. J. Chem.*, 1954, **32**, 366.