486. The Preparation and Dimerization of Methylketen.

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An account is given of the preparation of methylketen by pyrolysis of propionic anhydride vapour at low pressures and 400—600°. The compound readily dimerizes in the gas phase by a second-order reaction which occurs on the surface of the reaction vessel; the kinetics of dimerization are reported and discussed.

ALTHOUGH keten has been known since 1907 when it was first prepared by Wilsmore (*J.*, 1907, **91**, 1938) its next higher homologue, methylketen, has received very little attention. This is undoubtedly because the methods used for the preparation of keten fail or give poor yields when applied to the next member of the series. Also, methylketen is extremely reactive, combining rapidly with water, organic acids, or itself, and for this reason has previously been detected only by analysis of the products of its reactions.

Keten can be obtained by the thermal decomposition of any compound containing the group $CH_3 \cdot CO$; substances commonly used—acetone (*Ber.*, 1910, **43**, 2821), acetic acid (U.S.P. 2,278,537; Bamford and Dewar, *J.*, 1949, 2877), ethyl acetate (U.S.P. 2,175,811), and acetic anhydride (B.P. 472,988)—give good yields, in some cases of 90% or over ("Organic Reactions," Vol. III, p. 111).

Staudinger attempted to prepare methylketen by the action of zinc shavings on α-bromopropionyl bromide (*Ber.*, 1908, **41**, 906; 1911, **44**, 535) but obtained a poor yield. Hurd and his co-workers (*J. Amer. Chem. Soc.*, 1913, **45**, 2167, 3095; *J. Org. Chem.*, 1945, **10**, 62) pyrolysed ethyl methyl ketone and treated their products with aniline. The propionanilide formed demonstrated that a very low yield of methylketen had been obtained. Pyrolysis of methyl propionate (B.P. 504,626; U.S.P. 2,175,811) has also been claimed as a method of preparation but no yield was stated.

Recently a good yield was obtained by pyrolysis of propionic anhydride at low pressures followed by condensation of undecomposed reactant together with products other than the keten in a Liebig condenser, methylketen being collected in a trap cooled in liquid air (Fr.P. 901,236).

In the present work an adaptation of the last method was found to give at least a 90% yield of fairly pure methylketen.

EXPERIMENTAL

Preparation.—The apparatus is illustrated in Fig. 1. Propionic anhydride was placed in the dropping funnel A, the space above evacuated, and the anhydride out-gassed. The whole system was then evacuated and anhydride allowed to drop slowly through T_1 and T_2 into the flask B heated in an electrothermal mantle to about 150°. The vapour passed through an electric furnace C kept at 400—600° where decomposition ensued, and the emergent gases were condensed in a trap D cooled in liquid air. A quartz tube which had a very thin carbon coating over the inner surface was used as reactor.

After the entire charge had been passed through the furnace trap D was allowed to warm to room temperature whilst E was cooled in liquid air. In this way methylketen was distilled into E and this trap was isolated as soon as distillation was complete. The residue in trap D consisted of propionic acid together with undecomposed anhydride. Analysis of this mixture showed that conversions up to 90% could be obtained by using a furnace temperature as high as 550° without serious decomposition of methylketen. This was the temperature normally employed with a propionic anhydride pressure of the order of 5 mm. Hg. The contact time was approx. 10^{-2} sec.

The density of liquid methylketen at its b. p. being assumed to be 1·0 and the volume obtained being measured it was evident that one molecule of anhydride decomposed to give one molecule of acid plus one molecule of keten, as with acetic anhydride (Szwarc, *Trans. Faraday Soc.*, 1951, **47**, 269).

Methylketen is a pale green liquid when condensed, with b. p. −56°/760 mm. The vapour is extremely disagreeable and causes a very unpleasant taste.

Dimerization.—Methylketen in trap E was allowed to warm and vaporize into the 2-l.

flask F with a mercury manometer attached, F being contained in a thermostatically controlled bath. At a given time H was closed; immediately the pressure began to decrease owing to dimerization and condensation of the dimer. The reaction was followed manometrically.

All taps were lubricated with Dow Corning Silicone High Vacuum Grease.

A number of different substances were used to coat the walls of the reaction flask to investigate the effect of surface.

Silicone fluid 1107 was deposited from solution in carbon tetrachloride and the flask subsequently dried. After three repetitions of this process the vessel was cured overnight at 100°.

Paraffin wax was deposited from a hot solution in carbon tetrachloride. After removal of the mother-liquor the flask was gently warmed to allow flow of wax over the surface.

Quinol was deposited from a hot solution in acetone.

A fraction of the dimer (Found : C, 62·2; H, 7·1. Calc. for $C_6H_8O_2$: C, 64·3; H, 7·1%) boiling below 60°/12 mm. had M (cryoscopic in benzene) = 114, and the fraction boiling above this temp. had M = 124 (the dimer requires M = 112). The residue from the distillation gave M = 226, corresponding to the value for the tetramer (224). It was necessary to make freezing-point measurements at a series of concentrations and extrapolate the results to infinite dilution since association occurred in benzene solution.

FIG. 1.
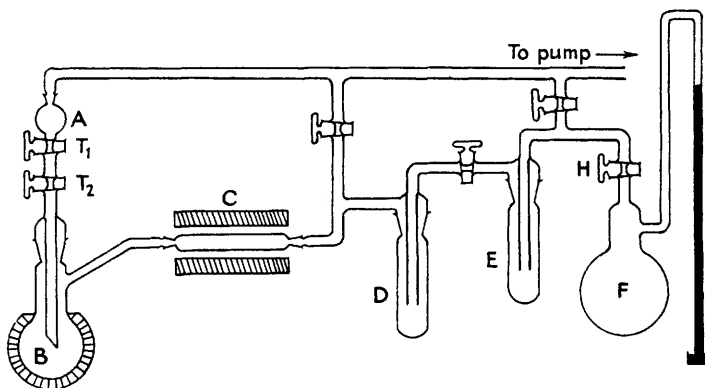
The results indicate that a high percentage of the product was dimer and a small quantity tetramer. It cannot be stated, at present, whether tetramer resulted from further polymerization of the dimer or from reaction between monomer and dimer. Dimer prepared by Sauer's method (*J. Amer. Chem. Soc.*, 1937, **69**, 2444) also contains fractions of higher molecular weight

RESULTS AND DISCUSSION

Unpacked Flask.—Preliminary experiments in an unpacked flask at 20° showed clearly that the dimerization reaction did not exhibit an integral order and moreover the runs were not reproducible to within more than a few per cent. In these experiments the vessel was not cleaned between runs, the accumulated volume of methylketen dimer being negligible.

Run	P_0 (mm. Hg)	$t_{0·5}$ (min.)	$t_{0·25}$ (min.)	$t_{0·5}/t_{0·25}$	Run	P_0 (mm. Hg)	$t_{0·5}$ (min.)	$t_{0·25}$ (min.)	$t_{0·25}/t_{0·25}$
B2	191	6·7	2·6	2·6	B5	213	5·2	2·0	2·6
B3	231	6·0	2·2	2·7	B6	212	5·1	2·0	2·5$_5$
B4	213	8·0	3·3	2·4	B7	195	3·5	1·3	2·7

For a reaction of the first order $t_{0·5}/t_{0·25}$ = 2 ($t_{0·5}$ is the half-life, $t_{0·25}$ is the quarter-life) whereas for a second-order reaction $t_{0·5}/t_{0·25}$ = 3. The annexed Table gives the values of these quantities for the first six runs (P_0 is the initial pressure).

To test the order of reaction for each individual run the half-life was measured for each of a series of pressures from the beginning of reaction to 20—30 mm., the initial pressure being of the order of 200 mm. For a second-order reaction the product of $t_{0·5}$ and initial pressure P_0 is constant, therefore $P_0 t_{0·5}$ was plotted against P_0 for each selected pressure.

If the reaction had been of second order throughout this would have given a straight line parallel to the P_0 axis. Of the above runs only those from B5 onwards gave a plot approaching linearity. Plots for B3 and B5 are presented in Fig. 2.

A few runs carried out at 0° appeared to show a higher rate of reaction than at 20°.

To test the indications that the reaction was partly or wholly heterogeneous the vessel was washed with acetone to remove the accumulated dimer and heated at 100° for two hours. The next run (C1) showed a suppressed rate for the first 10—15 minutes but successive runs did not exhibit this phenomenon. Pressure–time plots for C1, C2, and B5 are shown on Fig. 3. It is clear that for some minutes C1 followed an order lower than 2 before assuming the near-second order of previous runs. The plot of $P_0 t_{0.5}$ against P_0 for C1 (Fig. 2) demonstrates the tendency to approach second order as reaction proceeded.
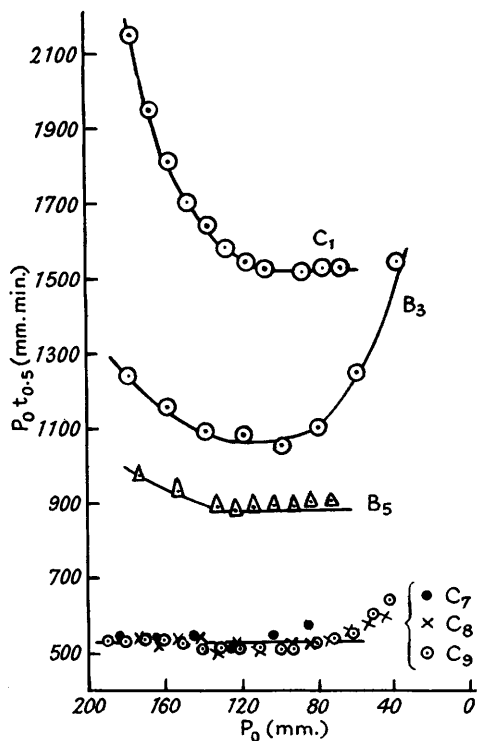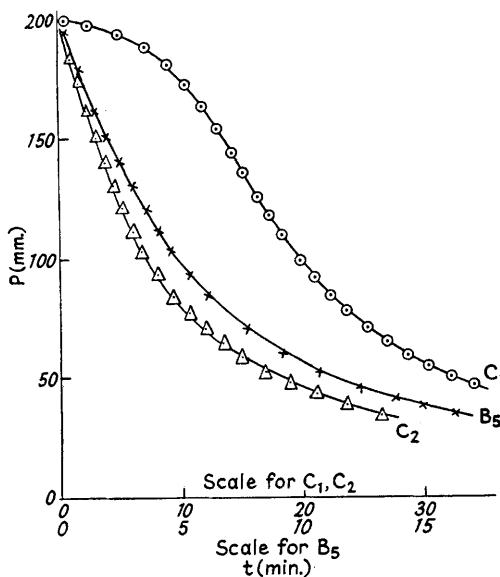

Fig. 2.

Fig. 3.

Packed Flask.—All subsequent experiments were carried out in the same reactor after it had been packed with 1″ lengths of Pyrex tubing of 3-mm. bore (apparent surface area increased by a factor 8). Again the first run (C6) (at 20°) showed a suppressed initial rate but C7, C8, and C9 display true second-order behaviour (see Table 1). A different reaction vessel, not otherwise used, gave a fourfold increase in rate when packed with glass wool.

In all cases plots of $P_0 t_{0.5}$ against P_0 showed that when the pressure had fallen below about 40 mm. the rate also fell rapidly, presumably owing to inability to maintain adsorption equilibrium.

For a second-order reaction $P_0 t_{0.5}$ is equal to the reciprocal of k_2, the rate constant in the equation, $d[M]/dt = k_2[M]^2$, where M = monomer. Thus the value at which the above plot approaches linearity gives the reciprocal of the rate constant. Since $1/k_2$ in the

TABLE 1. *Temp.* = 20°.

Run	Initial pressure (mm.)	$t_{0.5}$ (min.)	$t_{0.25}$ (min.)	$t_{0.5}/t_{5.20}$
C7	192·5	3·0	1·0	3·0
C8	190	3·2	1·1	2·9
C9	211·5	3·0	1·0	3·0

packed reactor was $1 \cdot 02$ l. mole^{-1} sec.$^{-1}$ (C7—9) and in the unpacked reactor $0 \cdot 31$ l. mole^{-1} sec.$^{-1}$ (B5) the effect of packing was to multiply k_2 by a factor $3 \cdot 5$ approximately. After the flask had been washed with acetone and dried a suppressed rate was again found at the start of the first run but subsequent runs gave the same rate constant as C7—C9. Thus the effect of acetone washing was to clean the surface of the glass in a reproducible manner.

Additional confirmation of the second-order nature of the steady reaction was obtained from plots of $1/P$ against time for each of the runs where the steady state had been obtained, these being quite linear.
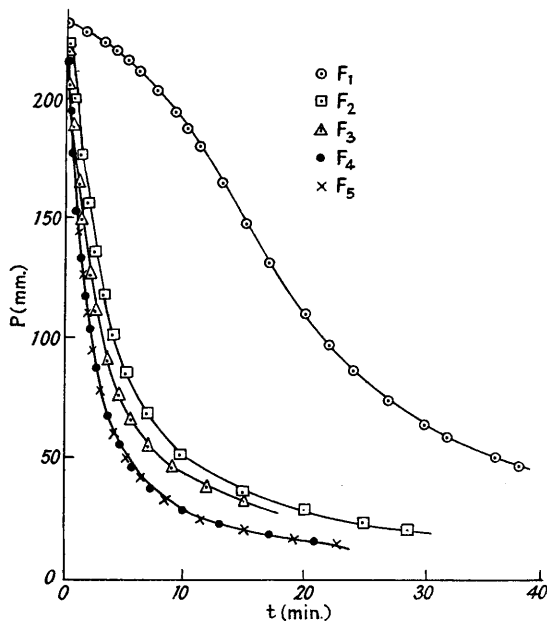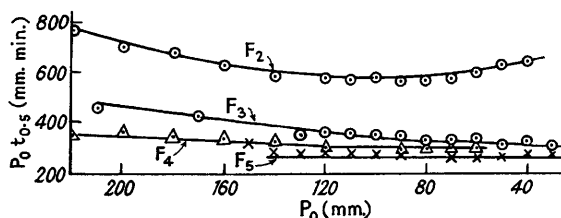
FIG. 4.

FIG. 5.

An attempt to determine the temperature coefficient of dimerization by altering the thermostat bath-temperature between successive runs gave poorly reproducible results. Several series of runs were therefore made, a clean acetone-washed flask being first used at each new temperature and runs being continued until they became of second order and showed a steady rate constant ; after 4—5 runs only a very slight increase in rate from run to run was observed, perhaps owing to polymerization occurring in solution in the accumulated liquid dimer. Runs F1—F5 are used to illustrate these trends and are typical. Fig. 4 presents pressure–time curves, and Fig. 5 plots of P_0 against $1/k_2$. Table 2 lists the k_2 values together with $t_{0 \cdot 5}$ and $t_{0 \cdot 25}$ for those runs which had achieved steady rate and order. Table 3 summarizes the temperature and rate data. The values of k_2 listed were obtained graphically from plots of $P_0 t_{0 \cdot 5}$ against P_0.

Consideration of the initial runs at various temperatures (Fig. 6) demonstrates the

reduction of initial rate with rise in temperature resulting in prolongation of the zero-order period of reaction.

Some runs were allowed to proceed for 2—3 days and in these cases residual pressure was always observed, amounting to 2—3% of the initial pressure of monomer at all temperatures employed. This must have been caused by an impurity in the methylketen but attempts to remove it by repeated distillation of the monomer at −80° were ineffective.

A surface coating of Silicone caused a greatly reduced initial rate in run L1 which should be compared with K1, both being made at 20° (Fig. 6). A coating of paraffin was without effect on the rate of reaction.

The possibility that the reaction followed a chain mechanism was investigated by direct visual observation. The type of chain mechanism specified below would lead to reaction occurring in the gaseous phase although remaining kinetically heterogeneous. For these experiments the monomer was introduced through an inlet tube leading to the

FIG. 6.
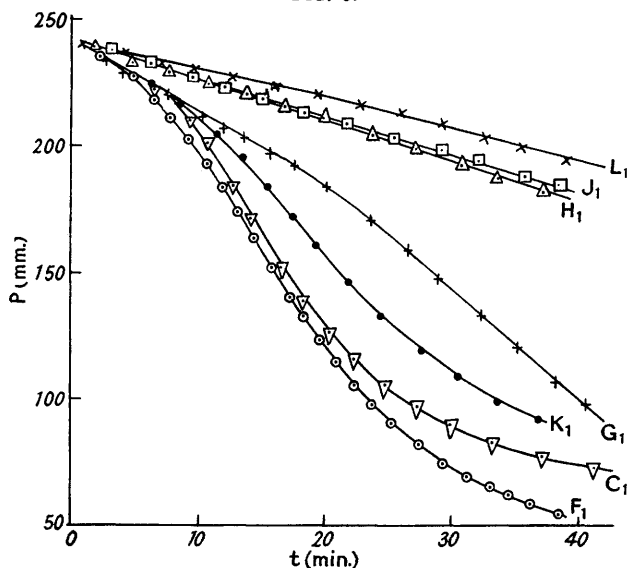
centre of the reaction flask, then a small portion of the vessel was warmed gently to remove the liquid condensed on it and the reaction was observed through this window. Reaction

TABLE 2.

Run	Initial pressure (mm. Hg)	$t_{0.5}$ (min.)	$t_{0.25}$ (min.)	$t_{0.5}/t_{0.25}$	k_2 (l. mole⁻¹ sec.⁻¹)	Temp. (c)
E5	206	1·55	0·4	3·3	1·50	0·0°
F2	221	—	—	—	0·52	30·3
F3	211	—	—	—	0·84	30·3
F4	220	—	—	—	0·98	30·3
F5	150	2·0	0·7	2·84	1·10	30·3
G2	220	—	—	—	0·26	62·1
G3	220	—	—	—	0·36	62·2
G4	180	3·8	1·2	3·16	0·46	62·4
H2	196	—	—	—	—	82·8
H3	206	—	—	—	0·24	82·8
H4	205	5·3	1·9	2·8	0·30	82·8
J3	172	—	—	—	—	94·7
J4	192	—	—	—	—	94·7
J5	202	7·5	2·3	3·25	0·22	94·7
K2	220	—	—	—	—	20·2
K3	180	—	—	—	0·75	20·2
K4	180	—	—	—	0·92	20·3
K5	110	2·7	0·9	3·0	1·02	20·3

Average 3·1

TABLE 3.

Run	k_2 (l. mole^{-1} sec.$^{-1}$)	Temp. (c)	Temp. (°K) (T_A)	$k_2 T_A$ (l. mole^{-1} sec.$^{-1}$)	$\log_{10}(k_2 T_A)$	$1/T_A$ (°K^{-1}) $\times 10^5$
E5	1·5	0·0°	273°	410	2·613	367
F5	1·1	30·3	303·3	332	2·521	330
G4	0·46	62·4	335·6	155	2·190	298
H4	0·30	82·8	355·8	107	2·029	281
J5	0·22	94·7	367·7	81	1·909	272
K5	1·02	20·3	293·5	299	2·476	340·5

occurred immediately at the walls where droplets of dimer formed, and also on the inlet tube but even though the walls were streaming with liquid dimer the gaseous phase remained completely clear and devoid of the mist which would have denoted dimer formation.

Two possible explanations of the second-order kinetics together with the heterogeneous effects might be suggested. (i) Adsorption of monomer followed by bimolecular reaction in the adsorbed phase. (ii) A chain reaction where initiation and/or termination occurred at the solid surface. The second-order behaviour could be accounted for in this case by the following scheme :

$$(1) \qquad M \longrightarrow X, \text{ or } 2M \longrightarrow X \qquad \ldots \ldots \quad k_1$$
$$(2) \quad X + M \longrightarrow D + A \qquad \ldots \ldots \ldots \quad k_2$$
$$(3) \quad A + M \longrightarrow X \qquad \ldots \ldots \ldots \ldots \quad k_3$$
$$(4) \qquad X \longrightarrow ?, \text{ or } 2X \longrightarrow ? \qquad \ldots \ldots \quad k_4$$
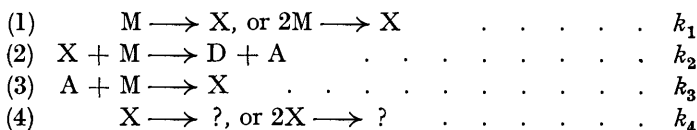
where M is the monomer, D the dimer, and X and A are intermediates. This scheme leads to :

$$-dM/dt = 2[M]^2 k_1 k_2/k_4 \text{ or } 2k_2[M]^2\sqrt{(k_1/2k_4)}$$

If (1) or (4) or both were wall reactions, heterogeneous effects would result. Since packing the vessel leads to an increase in rate it is unlikely that termination is a wall reaction, and the assumption remains that (1) is a heterogeneous process. This is contradicted by the indifference of the reaction to a surface layer of quinol, the rate being identical with that in the untreated vessel, and also by the apparent absence of dimer formation in the gaseous phase.

For these reasons alternative (i) above seems preferable.

Over the temperature range employed (0—95°) the dimerization followed a steady second-order course which was independent of temperature and pressure. These conditions are those which obtain when the apparent order is equal to the molecularity, the reaction being unretarded by the product (Hinshelwood, " Kinetics of Chemical Change," Oxford Univ. Press, 1947, p. 195).

Since the reaction is bimolecular it is envisaged that the rate-controlling step is reaction between two adsorbed molecules or between one molecule in the adsorbed phase and one in the gaseous phase, but the present results do not allow distinction to be made between these modes of reaction.

The activation energy found from a plot of $\log_{10}(k_2 T)$ against $1/T$ is $E = -3\cdot7$ kcal./mole. The function $k_2 T$ is used since θ, the fraction of available surface covered by adsorbed molecules, is a function of temperature. In fact the value of E obtained is not very sensitive to the power of T used in this calculation and the plot of $\log_{10}(k_2 T^{\frac{1}{2}})$ is almost identical in slope with the former. The fact that the activation energy is negative cannot be explained by a reversible dimerization leading to an equilibrium $2M \rightleftharpoons D$, since the residual pressure after infinite time was not dependent on temperature, but it is simply accounted for by the temperature dependence of adsorption.