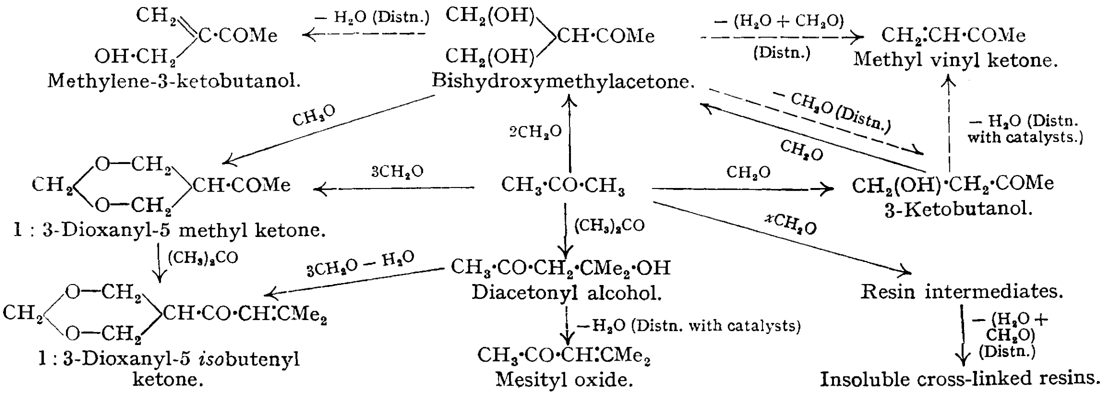
9. *The Preparation and Polymerisation of Methyl Vinyl Ketone.*

By Theodore White and Robert N. Haward.

Methyl vinyl ketone is of importance in view of its capacity for polymerisation to a thermoplastic resin. A detailed study has been made of the acetone–formaldehyde condensation with a view to establish the optimum conditions for the production of 3-ketobutanol, from which methyl vinyl ketone is obtained by dehydration. The condensation is complex and its various products are discussed and characterised. The preparation of pure methyl vinyl ketone has been studied, and its rate of polymerisation measured in a series of solvents. Both the high rate of polymerisation obtained in precipitants and the discrepancies observed in the kinetics of the polymerisation in benzene can be explained by the assumption that chain termination is retarded in liquids which do not dissolve the polymer.

The condensation of acetone and formaldehyde to 3-ketobutanol and the dehydration of the latter to methyl vinyl ketone were first reported by Merling and Köhler (B.P., 1909, 19087; *J. Soc. Chem. Ind.*, 1910, **29**, 1037). Later work, summarised by Morgan, Megson, and Pepper (*Chem. and Ind.*, 1938, **57**, 885), established that the condensation was a complex process and, with the present contribution, suggests that the reactions proceeding on condensation and subsequent distillation can be represented as in Fig. 1.

Fig. 1.



Little attention has been given to the isolation and purification of each component or to the manner in which variation of the condensation conditions affects the yield of 3-ketobutanol. It has, however, been claimed by Morgan *et. al.* (*loc. cit.*) and Rutovsky, Berlin, and Zabyrina (*J. Gen. Chem. Russia*, 1941, **11**, 550) that 3-ketobutanol enolises to form a terminal methylene group,

$$CH_2(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2(OH){\cdot}CH_2{\cdot}C(OH){:}CH_2,$$

and then polymerises under the influence of light or peroxides, a phenomenon not observed with other enols.

The necessity of obtaining pure methyl vinyl ketone before studying its polymerisation led to the present study of the acetone–formaldehyde condensation and to the elucidation of discrepancies in the earlier work. By methods such as those of Fenske, Tonsberg, Quiggle, and Cryder (*Ind. Eng. Chem.*, 1936, **28**, 644; 1937, **29**, 957) and Podbielniak (*Ind. Eng. Chem. Anal.*, 1933, **5**, 176), the condensation product left after removal of excess of acetone was thoroughly fractionated, thus giving details of the amounts of each component present and providing the products in a very pure state. This gave accurate physical constants for each product and an explanation of the " polymerisation " of 3-ketobutanol.

Earlier workers found that most of the condensation product resinified on distillation. Pressure variation, control of pH, and elimination of oxygen and peroxides did not prevent this, but by distillation in the presence of a high-boiling ester (butyl phthalate) it was found that the volatile components distilled without decomposition and the non-volatile products were precipitated unresinified from the cold ester. High-boiling paraffins did not show this effect, and the reason for the normal occurrence of resinification and its prevention by butyl phthalate remains obscure. The procedure permitted isolation of 70% of the crude product as volatile substances, which were refractionated without decomposition.

Application of this discovery established that a maximum yield of 3-ketobutanol was obtained by refluxing a 4 : 1 molar ratio of acetone : paraformaldehyde at pH 8·3—8·5 for a time just sufficient to permit complete reaction of the paraformaldehyde, the type and effect of variation of the condensation conditions being detailed in the Experimental section.

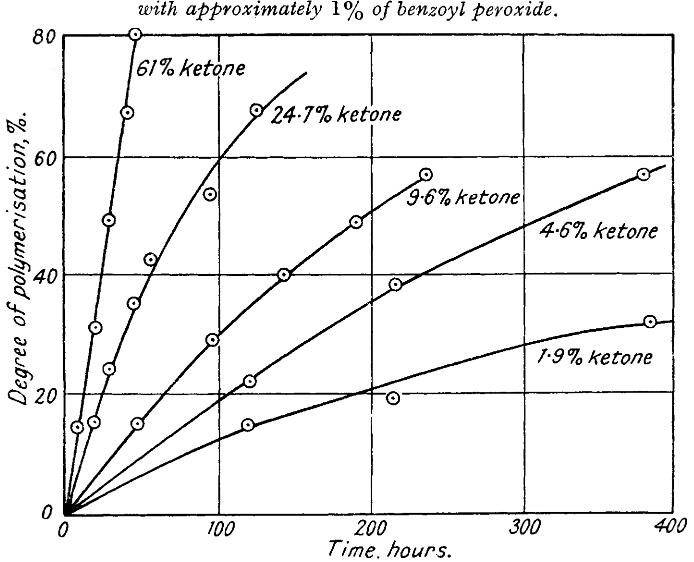
The product obtained under these conditions contained, after removal of the excess of acetone, 30% of non-volatile products, which were not investigated in detail, the volatile portion consisting of : (1) acetone; (2) water (together 9—10%); (3) diacetonyl alcohol, b. p. 63°/12 mm. (4—5%); (4) 3-ketobutanol, b. p. 70—71°/12 mm. (27—28%); (5) methyleneketobutanol, b. p. 82—83°/12 mm. (14—15%); (6) 1 : 3-*dioxanyl*-5 iso*butenyl ketone*, b. p. 90—92°/12 mm. (10—11%); (7) 1 : 3-dioxanyl-5 methyl ketone, b. p. 160°/12 mm. (3—4%).

Fractionation other than by the advanced technique cited gave a main, superficially pure fraction, b. p. 90—92°/12 mm.—the " 3-ketobutanol " of earlier workers. This was found to be a mixture of components (3)—(6), a fact which explains the supposed " polymerisation " of 3-ketobutanol. We have been unable to polymerise pure 3-ketobutanol of b. p. 70—71°/12 mm. and have no evidence of its enolisation. On the other hand, methyleneketobutanol, b. p. 82—83°/12 mm., polymerised with both light and peroxides, and its presence to the extent of some 30% in the mixture of b. p. 90—92°/12 mm. is sufficient to explain the 30% maximum yield of polymer obtained by Rutovsky *et al.* (*loc. cit.*) from their " 3-ketobutanol " and the similar polymerisation recorded by Morgan *et al.* (*loc. cit.*).

Of the components (1)—(7), the occurrence of diacetonyl alcohol and 1 : 3-dioxanyl-5 *iso*butenyl ketone has not previously been noted. The formulation of the latter rests upon analysis and cryoscopic molecular-weight determination (*M*, 165). Bromine absorption showed the presence of one double bond and a molecular weight of 160—170 ; and the production of acetone on oxidation with alkaline permanganate located this double bond in a terminal *iso*propylidene group. Hydroxylic oxygen was found to be absent, but although, like mesityl oxide and bishydroxymethylacetone, the substance did not give a bisulphite derivative, oxime, or phenylhydrazone, yet the presence of a keto-group was established by the formation of a 2 : 4-dinitrophenylhydrazone. With hot dilute acids formaldehyde was produced, indicating the presence of the remaining two oxygen atoms in a methylenedioxy-group. These facts can be interpreted by more than one formula, but all require the presence in the molecule of a substituted 1 : 3-dioxan ring. Morgan and Holmes (J., 1932, 2667) established the presence of an allied substance, 1 : 3-dioxanyl-5 methyl ketone, in this same condensation, and Morgan and Griffith (J., 1937, 841) found a similar type of product in the methyl ethyl ketone–formaldehyde condensation product. The formulation of product (6) as 1 : 3-dioxanyl-5 *iso*butenyl ketone is tentative, but the established presence in the condensation mixture of 1 : 3-dioxanyl-5 methyl ketone, from which it can easily arise by condensation with acetone (cf. the formation of diacetonylacetone), makes this the most likely of the alternatives.

FIG. 2.

The polymerisation of methyl vinyl ketone in benzene solution at 25° with approximately 1% of benzoyl peroxide.



The preparation of methyl vinyl ketone by dehydration of pure 3-ketobutanol and of the crude condensation mixture was also studied, the results explaining why its b. p.'s have been quoted as 74—87°/760 mm. Dehydration of 3-ketobutanol gave a constant-boiling methyl vinyl ketone–water mixture of b. p. 75°/760 mm. Dehydration of the crude reaction product gave ternary acetone–methyl vinyl ketone–water mixtures, which distilled as pseudo-constant-boiling fractions at any temperature from 69° to 94°/760 mm. according to the type and amount of dehydrating agent used. Refractionation always gave a ternary constant-boiling main fraction, b. p. 73—74°/760 mm., containing 42·5% of acetone, 42·5% of methyl vinyl ketone, and 15% of water, from which pure methyl vinyl ketone, b. p. 81·4°/760 mm. (corr.), $d_{25^\circ}^{25^\circ}$ 0·842, n^{15° 1·4120, was obtained by adding acetic anhydride to eliminate the water, the resultant acetone–methyl vinyl ketone–acetic acid mixture being readily separated into its pure components by a Fenske column. The methyl vinyl ketone so prepared was used in the following study of its polymerisation.

Polymerisation of Methyl Vinyl Ketone.—The pure ketone polymerised to a solid *d* 1·12, *i.e.*, with a 25% reduction in volume. Such volume changes have frequently been made a measure of the degree of polymerisation (*e.g.*, Bolland, *Proc. Roy. Soc.*, 1941, *A*, **178**, 24), and the method was used throughout this work, consistent results being obtained. The ketone polymerised slowly in the presence of benzoyl peroxide at room temperature and more quickly at 60°. Oxygen appeared to cause an induction period if there was less than 0·1% of peroxide present but the effect was not investigated in detail. The dilatometric method was not convenient for investigation of the undiluted monomer, since the polymer–monomer solution became nearly solid when only 20—30% of the monomer had polymerised, and the following results were all obtained in solvents.

Polymerisation in Benzene.—Polymerisation–time curves for benzene solutions of various concentrations, each containing approximately 1% of catalyst, are given in Fig. 2. For concentrations below 30% the curves are smooth and convex, as if the reactions were following first- or second-order kinetics. Table I illustrates for three concentrations of ketone the result of applying the usual relationships to these curves. The results are remarkable in that, if constancy of the velocity " constant " (*k*) during any individual reaction is taken as the criterion, the reaction is of first or 3/2 order, whereas if constancy of the velocity " constant " for various initial concentrations is the criterion, then the result is intermediate between a 3/2 and a second-order reaction. Clearly, the reaction cannot be assigned to any definite order.

TABLE I.

Velocity Constants for the Polymerisation of Methyl Vinyl Ketone in Benzene (first-, 3/2-, and second-order constants).

Ketone, 28·7% by vol. = 3·48 g.-mols./l.; benzoyl peroxide, 0·83% = 3·4 × 10^{-2} g.-mol./l.								
Time, hrs.	11.	19.	30.	47.	71.	95.	119.	143.
$10^4 k_1$	41	39	40	40	37	31	33	34
$10^4 k_{3/2}$	26	26	26	28	26	27	26	28
$10^4 k_2$	29	25	30	33	33	36	36	40
Ketone, 9·6% by vol. = 1·14 g.-mols./l.; benzoyl peroxide, 1·0% = 4·1 × 10^{-2} g.-mol./l.								
Time, hrs.	24.	48.	72.	96.	120.	144.	168.	192.
$10^4 k_1$	12·5	15	15	16	15	16	15	15
$10^4 k_{3/2}$	16	17	18	19	18	19	19	20
$10^4 k_2$	31	32	34	38	38	40	41	43
Ketone, 1·9% by vol. = 0·23 g.-mol./l.; benzoyl peroxide 0·99% = 4·1 × 10^{-2} g.-mol./l.								
Time, hrs.	216.	384.	600.	880.	1,296			
$10^4 k_1$	4·3	4·3	4·4	4·2	3·8			
$10^4 k_{3/2}$	11	11	13	13	12			
$10^4 k_2$	44	53	62	67	71			

This point is further emphasised by Table II, which gives a complete series of constants for the range 0·49—36·7% of methyl vinyl ketone (by vol.), the most satisfactory constant for each individual reaction being italicised. The results at the lowest concentrations are the least accurate, since the volume changes measured were very small. The results will not be discussed here, but it may be noted that a similar result was recorded for the polymerisation of vinyl acetate in toluene solution by Cuthbertson, Gee, and Rideal (*Proc. Roy. Soc.*, 1939, *A*, **170**, 315).

TABLE II.

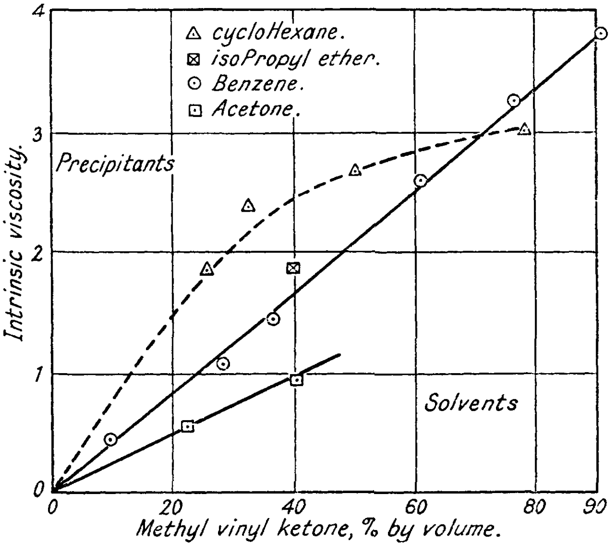
Velocity Constants for the Polymerisation of Methyl Vinyl Ketone in Benzene at 0·49—36·7% *by Vol.* (0·059—4·4 *g.-mol./l.*).

Approximately 1% *Catalyst throughout.*

Concn., g.-mols./l.	0·059.	0·23.	0·55.	1·14.	3·48.	4·4.
$10^4 k_1$	2·8	4·2	*9·0*	*15*	37	40
$10^4 k_{3/2}$	*15*	*12*	16	18	*27*	*29*
$10^4 k_2$	130	60	70	38	40	39

FIG. 3.

Intrinsic viscosity of methyl vinyl ketone polymers formed in various solvents at 25° *with approximately* 1% *of benzoyl peroxide.*



Changes in Intrinsic Viscosity.—Fig. 3 depicts the intrinsic viscosities (η_i) (cf. Gee, *Trans. Faraday Soc.*, 1940, **36**, 1167) of methyl vinyl ketone polymers formed in benzene and other solvents in the presence of approx. 1% of benzoyl peroxide. The results show that for benzene solutions the final viscosity is approximately proportional to the initial concentration of ketone. Hence it may be concluded that this variation in chain length will, of itself, introduce a factor proportional to the concentration of the ketone into any kinetic equation and therefore will raise the order by unity. If the evidence given above were taken as implying a first-order reaction, all the other processes would have to be zero order as far as the ketone concentration is concerned.

TABLE III.

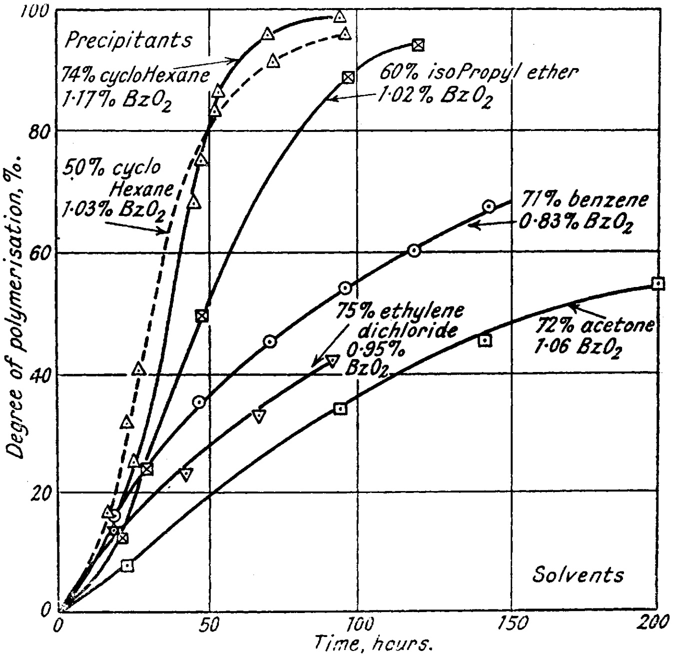
The Effect of Catalyst Concentration on the Polymerisation of Methyl Vinyl Ketone.

Ketone, g.-mols./l.	3·5	3·2	3·5	3·7	3·9
Catalyst (C_0), g.-mol./l.	0·034	0·0145	0·0062	0·0027	0·0013
$10^3 k_1$	3·7	2·1	1·9	1·2	0·92
$10^3 k_1 \times 1/\sqrt{C_0}$	20	18	24	23	26
Intrinsic viscosity	1·08	1·42	1·83	3·0	3·1
Intrinsic viscosity $\times \sqrt{C_0}$	0·20	0·17	0·14	0·16	0·11

The Effect of Catalyst Concentration.—These results suggested that any investigation of the effect of catalyst concentration should be carried out at a single concentration of ketone, whereby the effects due to the uncertain order of the reaction would be largely eliminated. In Table III the first-order constant (k_1) is given, in these circumstances, purely as an estimate of the rate of reaction. The results show that the rate of reaction is proportional to $\sqrt{C_0}$, as is usually the case for these catalysed polymerisations (cf. Cuthbertson *et al.*, *loc. cit.*; Schultz and Husemann, *Z. physikal. Chem.*, 1938, *B*, **39**, 246; Price and Kell, *J. Amer. Chem. Soc.*, 1941, **68**, 798), and it may be concluded that the reaction chain is terminated by a process of mutual saturation. The fact that the product, chain length $\times \sqrt{C_0}$, is much less constant and falls at low concentrations of the catalyst suggests that the reaction chain and the polymer chain may not always be synonymous and that a process of chain transfer such as that postulated by Kamenskaya and Medvedev (*Acta Physicochim.*, 1940, **13**, 565), occurs.

FIG. 4.

Polymerisation of methyl vinyl ketone in various solvents at 25° with approximately 1% of benzoyl peroxide.



The Effect of Variation of the Solvent.—Fig. 4 depicts the polymerisation of methyl vinyl ketone in a series of solvents; it is obvious that the rates of reaction differ widely, particularly in the later stages. This difference appears to be correlated with precipitation of the polymer in the same way as that observed for methyl methacrylate by Norrish and Smith (*Nature*, 1942, **150**, 336). In both *cyclo*hexane and *iso*propyl ether only the monomer is soluble, the polymer being precipitated as soon as any quantity is formed, whereas both acetone and ethylene dichloride are good solvents for the polymer. Reference to Fig. 3 shows that the solvents which give the highest reaction rates also give the longest chain lengths, but the difference in the rate of reaction is greater than that in molecular weight.

In view of the complex nature of the curves, no attempt has been made to analyse the reaction in *cyclo*hexane or *iso*propyl ether, but the reactions in ethylene dichloride and in acetone appear to give satisfactory

3/2- and second-order constants, respectively, as may be seen in Table IV. No allowance has been made for decomposition of the benzoyl peroxide in any of these reactions. It is certainly slow at 25°, but it could easily be fast enough to affect the kinetics of the longest reactions (50 days). The fact, however, that consistent kinetics are given in ethylene dichloride after this time suggests that the decomposition cannot be large and, in any case, the inconsistencies obtained with benzene cannot be attributed to this cause.

TABLE IV.

Velocity Constants for the Polymerisation of Methyl Vinyl Ketone in Acetone and in Ethylene Dichloride. [*Constants corrected for small deviations of* C_0 *from* 0·041 *g.-mol./l.* (1%), C_0 *being assumed low.*]

Acetone.

Ketone, g.-mol./l.	1·0	2·7	3·4	4·75
$10^3 k_2$	1·5	2·5	1·9	1·9

Ethylene dichloride.

	Methyl vinyl ketone = 0·16 g.-mol./l.						Methyl vinyl ketone = 3·0 g.-mols./l.			
Time, hrs.	120	316	384	600	888	1296	19	43	67	91
$10^3 k_{3/2}$	2·4	3·0	2·3	2·5	2·5	3·3	3·0	2·0	1·9	2·0

Discussion.—The results in different solvents are in agreement with those of Norrish and Smith (*loc. cit.*) and can be explained on similar lines—that precipitation reduces the rate of chain termination and hence increases the rate of reaction. The fact that the polymer chain length is not equivalently increased shows that the interaction of two active polymer chains plays a more important part in terminating the reaction chains than the polymer chains, *i.e.*, that chain transfer occurs.

This precipitation theory can also be extended to cover the irregularities in the kinetics of polymerisation in benzene, which is a poor solvent for the polymer. Here the accumulation of micellar aggregates may cause a similar rise in the rate of reaction as the polymer is formed and so cause a single reaction to appear of lower order than it really is. The theory would, however, appear to predict that the rate of polymerisation would be faster in a viscous solution of pure polymer than in a pure solvent. To test this, an experiment was made in acetone, since the polymer could not be dissolved in benzene, and it was found that in a 3% solution of polymer of $\eta_i = 2{\cdot}6$ the rate of reaction was the same as in the pure solvent. An explanation of this apparent discrepancy may be that the increase in viscosity when a small amount of polymer is present in a good solvent does not affect the agitation of the different parts of a single chain, which is the most important factor in the termination process, although it may reduce the rate of diffusion of the centre of gravity of the chain. It seems probable, however, that some factor of the viscosity type does play a part in the reaction owing to the relative ease with which simple monomeric substances polymerise to hard materials with very small internal monomeric concentrations.

Although the kinetics of the polymerisation cannot be ascertained with certainty, it seems probable that a bimolecular reaction takes place in benzene and acetone which can be consistently explained as :

Initiation : $\mathrm{M} + \mathrm{Catalyst} \longrightarrow \mathrm{Complex}$
$\mathrm{Complex} + \mathrm{M} \longrightarrow \mathrm{Chain} + \mathrm{Catalyst}$
Termination : $\mathrm{P}_r^+ + \mathrm{P}_s^+ \longrightarrow \mathrm{P}_r + \mathrm{P}_s$ (dead polymer)
Continuation : $\mathrm{P}_r + \mathrm{M} \longrightarrow \mathrm{P}_{r+1}$; rate $\propto [\mathrm{P}^+][\mathrm{M}]$
i.e., chain length is proportional to [M].

Together, these give the rate of reaction as proportional to $\sqrt{C_0}[\mathrm{M}]^2$.

The relation of chain length to concentration is, however, an uncertain factor which may account for the 3/2 order in the case of ethylene dichloride. Alternatively, it may be possible for this solvent to play the part of one of the monomer molecules in the initiation mechanism.

The results do not justify more detailed attention to the reaction mechanisms.

EXPERIMENTAL.

Fractionation.—Fractionations were carried out with Fenske columns (*loc. cit.*) and a total-condensation still-head, using a 10/1 reflux ratio and a distillation rate of 1—3 g./min. The column for atmospheric-pressure distillations had an internal diameter of 14 mm. and was packed for 50 cm. with 3 mm. diameter single helices made from 26-gauge nickel wire. Reduced pressure distillations were conducted with a similar type of column of 25 mm. internal diameter packed for 45 cm. with 6 mm. helices. The Podbielniak (*loc. cit.*) type of column was used for comparative purposes and gave identical results.

3-*Ketobutanol.*—3 L. of acetone, 315 g. of paraformaldehyde, and 20 ml. of 2N-methyl-alcoholic potash (pH = 8·3—8·5) were refluxed with mild stirring until 4 drops of the reaction mixture gave no reaction with 2 ml. of Tollens's reagent (*ca.* 5 mins.), indicating complete reaction of the paraformaldehyde. The reaction mixture was then neutralised with 2N-hydrogen chloride in acetone, and the excess of acetone distilled off on a water-bath until the distillation ceased (recovery = 2365 ml.), leaving the crude condensation product (800 g.). 500 Ml. of butyl phthalate were added to this product, and the mixture distilled under reduced pressure, volatile products distilling up to 180°/15 mm. (575 g.). The remaining non-volatile components of the crude product were precipitated when the butyl phthalate residues cooled.

The distillate was fractionated with the specified Fenske column, the third distinct fraction being 3-ketobutanol, b. p. 70—71°/12 mm., $d_{25^\circ}^{25^\circ}$ 1·029, n^{15° 1·435; yield 215 g., 23% (Found : C, 54·2; H, 9·0; OH, 18·9. Calc. for $C_4H_8O_2$: C, 54·5; H, 9·1; OH, 19·3%). It did not polymerise with peroxides or U.V. light or on exposure to ordinary light for

12 months. Contrary to the statement of earlier workers, it boiled without decomposition (b. p. 182°) at 760 mm. It gave a bisulphite derivative, resinified with alkalis, and was dehydrated to methyl vinyl ketone by numerous dehydrating agents.

Composition of the Crude Condensation Product.—Many samples of crude product prepared as above were fractionated thoroughly, only slight variations being noted. A typical 800-g. sample distilled from butyl phthalate gave 225 g. of non-volatile precipitate and 575 g. of volatile products. Fractionation of the latter gave the fractions: (i) b. p. 15—45°/50—20 mm., 80 g. (9—10%), *i.e.*, water and acetone; (ii) b. p. 63°/12 mm., n^{15° 1·4225, 33 g. (4—5%); (iii) b. p. 70—71°/12 mm., 215 g. (27—28%), 3-ketobutanol (cf. above); (iv) b. p. 82—83°/12 mm., $d^{25^\circ}_{25^\circ}$ 1·06, n^{15° 1·4675, 110 g. (14—15%); (v) b. p. 90—91°/12 mm., n^{15° 1·4720, 80 g. (10—11%); (vi) b. p. 160°/12 mm., 25 g. (3—4%).

Fraction (ii) was diacetonyl alcohol, formed by condensation of two acetone molecules; it had b. p. 164°/760 mm., and with acids or iodine gave mesityl oxide, b. p. 129°/760 mm., n^{15° 1·4435, with the smell of peppermint and other characteristics of this compound. Fraction (iv) consisted of methylene-3-ketobutanol; it absorbed bromine immediately (94% of the theoretical quantity) and had the characteristic properties of an ethylenic ketol, giving a bisulphite derivative and an acetate, b. p. 95°/25 mm., n^{15° 1·4530, and conformed with the product finally described by Gault and German (*Compt. rend.*, 1936, **203**, 514) as having b. p. 84—88°/13 mm. It polymerised slowly under the influence of light or peroxides to a product of low molecular weight (Found: C, 59·7; H, 8·5; OH, 18·0. Calc. for $C_5H_8O_2$: C, 59·4; H, 8·9; OH, 18·0%). The acetate (bromine absorption = 97% of the theoretical) polymerised similarly but much more slowly. Fraction (v), believed to be 1 : 3-*dioxanyl*-5 iso*butenyl ketone*, gave a 2 : 4-dinitrophenylhydrazone but no oxime or bisulphite derivative. It could not be acetylated. Analysis indicated the empirical formula $C_3H_{4\cdot5}O$, and bromine absorption (one double bond being assumed) a molecular weight of 177 [Found: C, 63·7; H, 8·0; *M* (Rast), 165. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%; *M*, 170]. Oxidation with cold alkaline permanganate gave acetone (somewhat less than 1 equiv.), identified after distillation from the reaction mixture as its 2 : 4-dinitrophenylhydrazone and estimated by the iodoform reaction. Treatment with hot 2N-hydrochloric acid split off formaldehyde (1 equiv.), estimated as its phloroglucinol condensation product (Morgan and Griffith, *loc. cit.*). The occurrence of this fraction has not been previously noted. Fraction (vi) corresponded in such details as were available with the 1 : 3-dioxanyl-5 methyl ketone described by Morgan *et al.* (*loc. cit.*) and previously designated " a methylene dioxy derivative."

The non-volatile product (Fraction vii), precipitated on cooling the butyl phthalate residues, was isolated by adding an equal volume of ether and filtering off the product, which was washed with ether and dried, giving a pale yellow amorphous powder; yield 225 g. (28—29%). This product resinified on distillation even at 0·0001 mm.; it was soluble in acetone, alcohol, chloroform, and ethyl acetate, but not in ether or light petroleum. Fractional precipitation indicated it to be non-homogeneous, and viscosity determinations on solutions of the material indicated a low average molecular weight. It was not further investigated.

Condensation Conditions and the Yield of 3-*Ketobutanol.*—The conditions giving a maximum yield of 3-ketobutanol have already been described. The use of different acetone–paraformaldehyde ratios, of other condensation temperatures, pH values, times of condensation, or of gradual addition of the paraformaldehyde, all gave lower yields of 3-ketobutanol due to incomplete condensation or excessive resin intermediate formation according to the factor involved. Paraformaldehyde was preferable to formalin, reagent purity (within normal limits) had little effect, and the alkalis were the best catalysts for the condensation. The adverse effect of varying one factor could not be completely compensated by varying another. Details of all the experiments carried out cannot be given, but Table V gives the results of a number of comparative experiments designed to elucidate the effect of variation of the condensation conditions upon the yield of 3-ketobutanol. All the condensations were carried out with 315 g. of paraformaldehyde and, except where stated, a 4 : 1 molar ratio of acetone : paraformaldehyde—the reactions being conducted at the b. p. of the mixture with 2N-methyl-alcoholic potash as catalyst except where otherwise indicated.

TABLE V.

Illustrating the Effect of Condensation Conditions on the Yield of 3-*Ketobutanol.*

Molar ratio, $COMe_2/(CH_2O)_n$.	2N-MeOH–KOH, ml.	pH.	Time of condensation (mins.).	Yield, g.	Remarks.
4/1	9	7·5	5	112 *	Incomplete condensation
,,	11	7·8	,,	183	Maximum efficiency at pH 8·3—8·5; higher pH lowers yield by increasing resin intermediate formation
,,	15	8·0	,,	194	
,,	17	8·3	,,	212	
,,	20	8·5	,,	220 *	
,,	22·5	8·8	,,	169	
,,	25	9·2	,,	147	
,,	40	10·0	,,	122 *	
,,	9	7·5	60	86	Compare with 5-min. results marked *
,,	20	8·5	,,	160	
,,	40	10·0	,,	65	
2/1	20	9·3	5	65	pH changes complicate but do not disguise trend of the results
3/1	20	8·9	,,	104	
4/1	20	8·5	,,	215	
7/1	20	8·0	,,	192	
4/1	5 ml. C_5H_5N	—	360	0	No condensation
,,	20 g. $Ca(OH)_2$	7·5	120	180	Complete condensation in both cases
,,	60 g. K_2CO_3	7·5	120	90	

Methyl Vinyl Ketone.—The crude product (800 g.) from a condensation such as that above was heated with 80 g. of concentrated phosphoric acid, the distillate being fractionated through a Fenske column as it was produced; the main fraction distilled at 73—74°/760 mm.; n^{15° 1·39—1·406; yield 200 g. Refractionation gave back the same product—a ternary acetone–methyl vinyl ketone–water mixture in the ratio 3 : 3 : 1. This was treated with an equal weight of acetic anhydride, kept at room temperature for 24 hours to remove water, and then refractionated, giving sharp acetone, methyl vinyl ketone, and acetic acid fractions. The methyl vinyl ketone so obtained was a colourless, lachrymatory liquid, b. p. 81·4°/760 mm. (corr.), n^{15° 1·4120, $d^{25^\circ}_{25^\circ}$ 0·842; yield 95 g., *i.e.*, 54% on the 3-ketobutanol in the crude product or 13% overall yield.

Dehydration of pure 3-ketobutanol in the above manner gave a methyl vinyl ketone–water binary mixture, b. p. 75°/760 mm., which again required acetic anhydride treatment before the pure ketone could be isolated. The product, again produced in a 55% yield, was identical with that above. No further purification of this product was possible nor were any impurities detected. The pure ketone polymerised readily to a hard colourless resin which absorbed water readily to give the soft rubbery polymer generally described.

The Effect of varying the Type and Amount of Dehydrating Agent.—A number of dehydrating agents were used to convert 3-ketobutanol and the crude condensation product into methyl vinyl ketone. Each produced a main fraction with its own characteristic constants, the product in all cases giving the same ternary mixture of b. p. 73—74°/760 mm., η^{15° 1·39—1·4006, on refractionation. Some of the results are listed below, dehydration being combined with fractionation through a Fenske column in each case. For routine work, 10% phosphoric acid was added, since it gave the product closest to that given by refractionation. The yield of ketone varied but slightly with the dehydrating agent used.

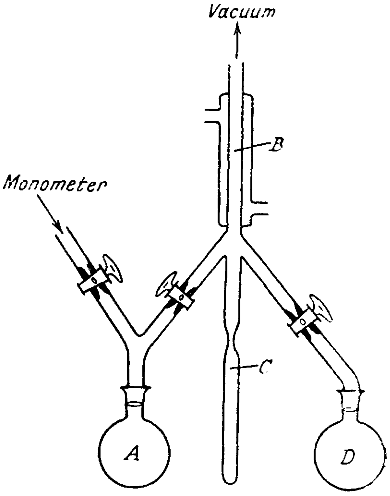
Dehydrating agent.	Proportion, %.	B. p. of product.	*n*.
H_3PO_4	1	89—92°	1·399 —1·3995
,, ...	10	73—74	1·39 —1·4006
H_3PO_4 + NaCl	1 + 7	72—74·4	1·3998—1·4048
$CaCl_2$	7	92—94	1·3821—1·3954
HCl	1	70—73°	1·3882—1·4004
HCl + NaCl ...	1 + 7	71—74	1·3901—1·4030
HCl + $CaCl_2$ ...	1 + 7	68—71	1·3825—1·4008

Condensation Conditions and the Yield of Methyl Vinyl Ketone.—The yield of ketone varied with the condensation conditions in the same way as did that of 3-ketobutanol, the data below showing the lower yield of product and higher pH required on carrying out the reaction at room temperature instead of at the b. p.—the reaction being carried out with 3 l. of acetone and 315 g. of paraformaldehyde.

2N-MeOH–KOH, ml.	7·5	12	16	25	30
Yield of ketone, g. at 25°	incomplete condensation		30	72	60
Yield of ketone, g. at b. p.	20	78	85	61	57

Technique of investigating the Polymerisation of Methyl Vinyl Ketone.—The monomer was fractionated in nitrogen into flask *A* of the apparatus shown in Fig. 5, samples of b. p. 80·5—82° only being used. Flask *A* was then evacuated, the liquid being allowed to boil freely to carry away any dissolved gases in a stream of vapour. The liquid was then distilled into the condenser *B* so that it ran down into the calibrated tube *C* which already contained a weighed amount of catalyst and in which it could be sealed off. When dilute solutions were being investigated, *C* in some cases took the form of a thermometer with capillary and bulb. Before use, *C* was cleaned with chromic acid, acetone, and distilled water, and dried. Solvents were introduced when necessary from the flask *D*. The charged tube *C* was finally sealed, detached, and then attached to a laminated glass scale and immersed in a thermostat at 25°. Illumination was from behind the scale, and the readings took the form of observation of the downward movement of the meniscus in *C*.

Fig. 5.



Subsequent work on other monomers showed that the vacuum distillation of the monomer from *A* directly into the reaction tube was the most essential precaution for consistent results.

Solvents.—The solvents used were: Benzene, B.D.H., extra pure for molecular-weight determinations; *cyclo*hexane, B.D.H., spectroscopically pure; acetone, B.D.H., purified by sodium iodide; ethylene dichloride, purified by the method of Proskauer and Weissberger ("Organic Solvents," p. 157), b. p. 81·45—81·55°; *iso*propyl ether, technical, redistilled.

The authors express their gratitude to Messrs. Colmore Adhesives Ltd. for permission to publish these results.

Colmore Adhesives Ltd., Team Valley Trading Estate,
Gateshead-on-Tyne.

[*Received, November 5th*, 1942.]