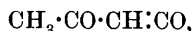


LXXXIX.—*Acetylketen: a Polymeride of Keten.*

By FRANCES CHICK AND NORMAN THOMAS MORTIMER WILSMORE.

It has been already stated (*Nature*, 1907, 75, 510; *Trans.*, 1907, 91, 1938) that keten, both in the liquid and the gaseous states, condenses on standing at the ordinary temperature to form a pungent-smelling brown liquid. This brown liquid has now been found to contain a new substance, which, as we hope to show in the present paper, is in all probability *acetylketen*, having the formula



and, consequently, standing in the same relation to acetoacetic acid as keten does to acetic acid.

As was to be expected, this condensation of keten takes place the more readily the purer and the more concentrated the keten is, and is therefore most conveniently brought about by allowing liquefied keten under pressure gradually to attain the temperature of the room. To carry out the operation, the crude keten is first roughly fractionated in the receiver of the apparatus, already described (*Trans.*, *loc. cit.*), in order to expel the bulk of the more volatile impurities. As soon as the boiling point has risen to -70° to -65° , the taps are closed, and the keten is frozen by means of liquid air. The receiver is then connected, on the one hand, to an exhaust pump and, on the other, to a manometer and to a thick-walled glass tube, closed at one end, and drawn off to a thick-walled capillary at the other. After the whole apparatus has been exhausted, the connexion to the pump is closed, and the keten is distilled over by removing the liquid air-bath from the receiver and applying it to the thick-walled tube. When all the keten has passed over, the thick-walled tube is sealed off.

It was mentioned in the previous paper that the spontaneous condensation of keten was accompanied by considerable evolution of heat. This was noticed first on handling one of the tubes about half an hour after it had been sealed up, when the end of the tube containing the liquid was found to be much too hot to hold. In order to follow the reaction more carefully, a sealed tube containing about 7 c.c. of liquid keten was placed, along with a thermometer, in a wide glass tube containing 50 c.c. of alcohol, which had been previously cooled to about -60° . The apparatus was placed in the open air, and was observed from a distance by means of a telescope. The keten remained colourless until the temperature of the bath had risen to 0° , when it

began slowly to turn brown. The reaction then went on with increasing rapidity, and the temperature of the bath gradually rose to 21° , remained at that point for about a quarter of an hour, and then slowly fell. The temperature of the air outside varied, meanwhile, between 10° and 7° . The reaction appeared to be complete after about three-quarters of an hour from the time when the keten began to turn brown. A second similar tube was placed in an air jacket and was observed as before. In this case a violent reaction, lasting for nearly five minutes, took place soon after the liquid began to turn brown. The heat of the reaction is therefore considerable. A quantitative determination of it by means of an ice calorimeter is contemplated.

On distilling the brown liquid, it was found to consist partly of a colourless liquid, which passed over between 125° and 127° , and partly of a brown residue, which is now being further examined. The yield of the colourless liquid was not very large, about 5 grams being obtained from 200 grams of acetic anhydride. On redistilling the colourless liquid under a pressure of 760 mm., it boiled at 126 – 127° with slight decomposition, a portion being always converted into some of the brown solid; but it could be distilled under reduced pressure (50–100 mm.) without change.

For analysis, the substance was weighed in a small stoppered bottle of hard glass, which was opened and placed in the boat as the latter was being pushed into the combustion tube.* The vapour density was determined by means of the Hofmann apparatus, using freshly-distilled *m*-xylene for the vapour jacket. In calculating the net pressure, allowance was made for the temperature of the mercury column, and for the vapour pressure of the mercury in the tube. Owing to the tendency of the vapour to polymerise, the result is rather high:

0.1419 gave 0.2938 CO_2 and 0.0614 H_2O . $\text{C} = 56.5$; $\text{H} = 4.8$.

0.1118 „ 0.2331 CO_2 „ 0.0500 H_2O . $\text{C} = 56.9$; $\text{H} = 5.0$.

0.0971 „ 71.4 c.c. at 139.3° and 409 mm. $\text{M.W.} = 85.8$.

0.4034 in 18.20 benzene gave a depression of 1.315° . $\text{M.W.} = 84.3$.

$\text{C}_4\text{H}_4\text{O}_2$ requires $\text{C} = 57.1$; $\text{H} = 4.8$ per cent. $\text{M.W.} = 84.0$.

The substance is therefore formed by the union of two molecules of keten.

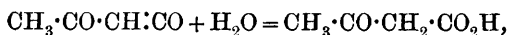
The liquid dissolved slowly on shaking with cold water, forming a strongly acid solution, which gave a deep violet colour with ferric chloride. On heating the aqueous solution, carbon dioxide and acetone were formed, the latter being recognised by means of the iodoform reaction, the alkaline mercuric chloride test, and the forma-

* The liquid was too volatile to weigh in the boat, and when placed in the usual bulb-tube the brown solid formed in the capillary on heating could not be completely burnt.

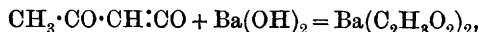
tion of the crystalline compound with benzaldehyde. Hydrogen chloride facilitated the dissolution and decomposition. On warming the substance or its aqueous solution with aqueous alkalis, it was decomposed, acetates being formed. The substance therefore combines with water to form acetoacetic acid.

The liquid was found to react with aniline with great energy; in fact, if the aniline was added too quickly, the mixture boiled. A crystalline substance was produced, which, after recrystallisation from alcohol, proved to be acetoacetanilide, melting at 84° . This was confirmed by heating a portion with excess of aniline, when carb-anilide (m. p. 235°) was formed.

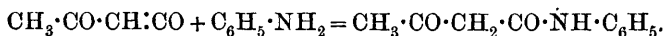
All the above reactions may be satisfactorily explained on the assumption that the new body is *acetylketen*. Thus with water we have:



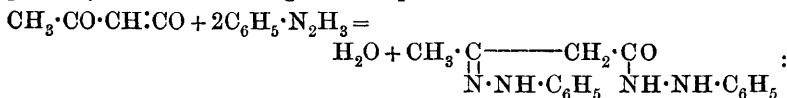
with alkalis:



and with aniline:



Acetylketen in benzene solution reacts with two molecular proportions of phenylhydrazine, yielding a substance which crystallised from alcohol or benzene in colourless plates melting with slight decomposition at 152° — 153° . Analysis showed that this substance had the composition of a *phenylhydrazone-phenylhydrazide*. It is probably formed according to the equation:



0.1156 gave 0.2877 CO_2 and 0.0677 H_2O . C = 67.9; H = 6.5.

0.1214 „ 0.3022 CO_2 „ 0.0705 H_2O . C = 67.9; H = 6.5.

0.1114 „ 19.67 c.c. moist nitrogen at 18° and 754 mm. N = 20.1.

0.1775 in 16.98 benzene gave an elevation of 0.095° . M.W. = 288.

$\text{C}_{16}\text{H}_{18}\text{ON}_4$ requires C = 68.1; H = 6.4; N = 19.9 per cent. M.W. = 282.

The substance dissolved readily in dilute hydrochloric acid, forming a very soluble hydrochloride, which gave a well-defined *platinichloride*.

Acetylketen differs markedly from keten in that it does not appear to react either with alcohols or with phenols, and this fact gave rise to the suggestion that it might be after all not a true keten, but an isomeride, such as diketotetramethylene.

To test this point the molecular refraction was determined, and the result was compared with the values calculated for the various isomeric formulæ from Conrady's numbers for the atomic refractions

for sodium light (*Zeitsch. physikal. Chem.*, 1889, 3, 210). The pyknometer contained 0.7433 gram of water weighed in air at 18°, 0.8143 gram of acetylketen at 18°, and 0.8118 gram at 23°; reducing to the vacuum and to the density of water at 4°, the density of acetylketen was accordingly $d_{18^\circ} = 1.0939$ and $d_{23^\circ} = 1.0905$. The refractive index, measured with a Pulfrich apparatus at 23°, using sodium light, was $n_D = 1.4342$, which from the Lorentz formula gives M.R. = 20.075. The calculated values are:

	M.R.
$\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}$	20.489
$\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}$	21.430
$\begin{array}{c} \text{CH}_2 \quad \text{CO} \\ \quad \diagdown \quad \diagup \\ \quad \text{CO} \\ \quad \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \end{array}$	18.782
$\begin{array}{c} \text{CH} \quad \text{C}(\text{OH}) \\ \quad \diagdown \quad \diagup \\ \quad \text{C}(\text{OH}) \\ \quad \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \end{array}$	20.664

Thus the acetylketen formula appears, according to this test also, to be the most probable, the only other formula which approaches it being that of the otherwise highly unlikely phenolic form of diketotetramethylene. There is, nevertheless, still a considerable difference between the calculated and the observed value for acetylketen, but, perhaps, this may be due to the oxygen in the terminal CO group having a lower atomic refraction than "aldehydic" oxygen in general. We hope to test this hypothesis shortly by determining the molecular refraction of keten itself.

As already mentioned, acetylketen is a colourless liquid at the ordinary temperature. On cooling sufficiently, it freezes to a white solid, which melts at -7° to -6° . It has an extremely pungent smell, differing entirely from that of keten, and suggestive at the same time of acetic anhydride and of acrolein. Its vapour attacks the eyes and the mucus membranes, but, like keten, it does not appear to leave any unpleasant after-effects. On standing at the ordinary temperature, even in absence of air, it gradually turns brownish-yellow. The change is, however, less rapid in Jena than in soda glass, and is in any case extremely slow at 0° . It would seem not to proceed very far even at the ordinary temperature, since a bomb tube which had been left sealed up for several months gave, when opened, practically the same yield as tubes freshly prepared. The boiling point, density, and refractive index have been already given. The dielectric constant has been measured for us by Dr. A. W. Stewart by means of the Drude apparatus, the value 16—17, or practically the same as that of acetoacetic ester, being obtained. The absorption spectrum of acetylketen was photographed by Mr. H. E. Watson, using solutions in dry ether and in alcohol up to 0.1*N*.

There was no absorption band, but a small general absorption in the ultra-violet resembling that produced by acetoacetic ester.

Acetylketen is readily miscible with all the usual organic solvents. It reacts violently with pyridine, forming a brown substance apparently identical with that which we have observed to be formed by the action of keten on pyridine. The pyridine seems to act merely as a catalytic agent, since it could be readily washed out from the mixture, leaving a residue free from nitrogen. The reaction proceeded much more slowly in benzene solution, the acetylketen being then almost entirely converted into dehydracetic acid, which, after crystallisation from alcohol and light petroleum, melted at 108.5° . On the other hand, acetylketen reacts slowly with quinoline, yielding a sparingly soluble, crystalline substance melting with decomposition at 231° , which, however, does not contain nitrogen. With sodium ethoxide in dry alcohol, acetylketen forms chiefly sodium ethylacetoacetate. This, on treatment with hydrogen chloride, gave carbon dioxide and a ketone, which was evidently methyl propyl ketone. Hydroxylamine hydrochloride has no action on acetylketen, but the latter combines readily with the free base in alcoholic solution. Hantzsch's methyliso-oxazolone was, however, not produced, but a very soluble, readily oxidisable, crystalline substance was obtained on evaporation.

We are continuing the investigation both of keten and of acetylketen, and we propose to study especially the action of Grignard's reagent on these substances.

Our thanks are due to Mr. H. T. Clarke, who kindly assisted in the carrying out of several of the experiments.

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