one-sixth of the vitamin G potency was shown by the filtrates after removal of the activated solids.

5. When the adsorption processes were carried out in an atmosphere of nitrogen rather than air and under otherwise comparable conditions, the activated solids were somewhat more potent in both vitamins B(B_1) and G and the filtrates were more potent in vitamin G. The apparent losses are being studied in other ways and in the light of the newer evidence as to probable multiple nature of vitamins B and G.

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Liquid Ketene and Ketene Polymers

BY CHARLES D. HURD, AMOS D. SWEET AND CHARLES L. THOMAS

In a study of liquid ketene which was prepared by liquefaction from the gas stream from the pyrolysis of acetone, a few new items of interest were found. (1). Polymerization, which occurs even at −80°, may be retarded by a trace of hydroquinone (2 mg. for 2 cc. of liquid). (2). No reaction was observed in twelve hours between liquid ketene and metallic sodium or sodium–potassium (1:2) alloy or sodamide (suspended in toluene) or isoprene. Thus, the alkali metals did not bring about rearrangement of ketene into hydroxyacetylene ($HC\equiv COH$) and the isoprene did not add in the way it adds to maleic anhydride.[1] Possibly the low temperature was a contributing factor in these negative effects. (3). An extremely vigorous reaction was observed between liquid ketene and the Grignard reagent. Even at −78° and diluted with ether the reaction with *n*-butyl- or phenylmagnesium bromide was so vigorous that each added drop of Grignard reagent produced a crackling sound. The voluminous yellow solid which precipitated hydrolyzed to a sticky gum from which nothing was obtained. This is a modification of the experiment of Deakin and Wilsmore.[2] They diluted gaseous ketene with hydrogen and observed a very complex reaction as it was passed into a cold ether solution of methylmagnesium bromide.

(4). Tertiary alcohols react with liquid ketene giving *tert*-alkyl acetates. In previous unpublished work,[3] it was demonstrated that ketene gas also acetylates these tertiary alcohols but less effectively. This confirms Davis and Murray[4] who stated: "Tertiary butyl acetate, a typical tertiary ester, is suitably prepared by the action of ketene with tertiary butanol." However, Davis and Murray cited no experimental work.

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(1) Diels and Alder, *Ann.*, **460**, 98 (1928); **470**, 62 (1929); **478**, 137 (1930).

(2) Deakin and Wilsmore, *J. Chem. Soc.*, **97**, 1968 (1910).

(3) Hurd and Martin, M.S. thesis of K. E. Martin, Northwestern University, 1928.

(4) Davis and Murray, *Ind. Eng. Chem.*, **18**, 846 (1926).

Six cc. of *tert.*-butyl alcohol (b. p. 79.5–80°) at 20° was added dropwise during ten minutes to 6 cc. of liquid ketene at −78°. The alcohol solidified but gradually dissolved. After three hours the mixture was distilled. About 3 cc. of the alcohol was recovered and 4.5 cc. of a *tert.*-butyl acetate fraction (92–98°) formed which, on redistillation, gave these constants: b. p. 96°; $n_D^{18.5}$ 1.386 as compared with the recorded value[5] of 1.3887.

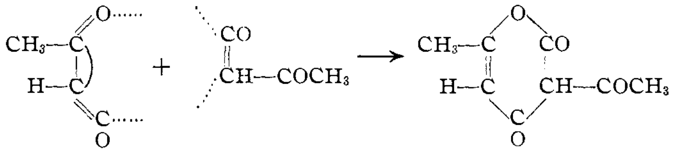
Similarly, 5 cc. each of *tert.*-pentyl alcohol and ketene were admixed and the mixture distilled after three hours. Three cc. was collected below 120° and 2.5 cc. above 130°. The *tert.*-pentyl acetate fraction, b. p. 120–130°, was 4.0 cc. On redistillation, it boiled at 123° (747 mm.); n_D^{20} 1.392.

Polymers of Ketene.—It was found that both ketene dimer and dehydroacetic acid were by-products in the preparation of ketene from acetone. Accordingly, an apparatus was constructed to facilitate the separation of these polymers. Acetone was boiled into the bottom of a vertical Pyrex reaction tube (2.5 × 90 cm.) the temperature of which was held at 700° by an electric furnace. The escaping gases were directed downward through a water cooled condenser and the condensate returned to the acetone flask to be recycled. The acetone which remained in the gas stream was separated with a coil condenser at −15°. When acetone was boiled into the apparatus at such a rate that 2 drops per second of condensed acetone fell from the water condenser, then the flow of ketene in the uncondensed gas was 0.3 mole per hour. Part of this ketene could be liquefied in a trap at −78° but for complete removal a liquid air trap was necessary.

Fractionation of the condensate to 70° at the end of a day's run left a residue weighing 30–50 g. From 15 liters of acetone, 300 g. of this residue was obtained. Two hundred grams of this was crude ketene dimer, b. p. 120–130°, and 100 g. was still higher boiling. Both fractions were contaminated with some acetic anhydride, the presence of which was no doubt due to the fact that the technical acetone used contains some water: $2CH_2CO + H_2O \longrightarrow (CH_3CO)_2O$. The identity of ketene dimer was confirmed not only by its boiling point, 125°, but also by its derivative with aniline, namely, acetoacetanilide, m. p. 84°.

The 100 g. of higher boiling residue was about two-fifths dehydroacetic acid. This was separated by two methods: (1) chilling in a refrigerator and recrystallization of the crystals thus produced from either water or benzene; (2) vacuum distillation. The melting point by either method was 108° and it was not depressed by mixing with known dehydroacetic acid. In the vacuum distillation of a 25-g. portion of the 100 g. of residue, 3 cc. of liquid distillate was collected, after which a 10-g. fraction appeared which solidified on cooling. This was dehydroacetic acid. The higher boiling residue was a brown tar which appeared to decompose as it was distilled further.

Chick and Wilsmore[6] obtained dehydroacetic acid[7] by treating ketene dimer with a little pyridine. This polymerization is most simply explained on the assumption that ketene dimer is acetylketene rather than cyclobutanedione. Using partial valence formulas it is a straightforward addition



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[5] Smith and Olsson, *Z. physik. Chem.*, **118**, 99 (1925).

[6] Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); **97**, 1987 (1910).

[7] For its structure, see Rassweiler and Adams, THIS JOURNAL, **46**, 2758 (1924).

The acetylketene formula may be reconciled with Chick and Wilsmore's observation that ketene dimer gives rise to γ-bromoacetoacetyl bromide on bromination by assuming the following rearrangement

$$CH_3COCHBrCOBr \longrightarrow CH_2BrCOCH_2COBr$$

That the —COBr group may facilitate this rearrangement is very reasonable in view of the similar rearrangement[8] which is promoted by the —$COOC_2H_5$ group: $CH_3COCHBrCOOC_2H_5 \longrightarrow CH_2BrCOCH_2COOC_2H_5$.

In a recent paper by Berl and Kullman[9] entitled "Preparation of Ketene by the Catalytic Decomposition of Acetone," acetone vapors were decomposed in an apparatus of the customary type.[10] One gains the impression that a pronounced catalysis was observed, but as a matter of fact any catalytic effects were very small. The yield of ketene depended in large measure on the temperature (about 700°, whereas for useful catalysis one might anticipate about 300 or 400°) and on the ratio of vaporized to decomposed acetone. The best yield (77%) was obtained at 680° with the above ratio as 22:1. The fact that a V_2O_5 filler was present in the reaction tube seems less important than Berl and Kullmann infer, for similar results were obtained[11] with about the same conditions when the reaction tube was quite empty.

Summary

Liquid ketene fails to react with sodium, sodium–potassium, sodamide or isoprene. Its reaction with Grignard reagents is violent and complex. Liquid ketene reacts satisfactorily with *tert*-butyl and *tert*-pentyl alcohols to give the *tert*-alkyl acetates.

Ketene dimer and dehydroacetic acid are by-products of the ketene synthesis. A method of isolating them is described.

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(8) Hantzsch, *Ber.*, **27**, 355, 3168 (1894).

(9) Berl and Kullmann, *ibid.*, **65**, 1114 (1932).

(10) "Organic Syntheses," John Wiley and Sons, New York, 1932, Collective Vol. I, p. 326.

(11) Hurd and Dull, THIS JOURNAL, **54**, 3428 (1932).