[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Ketene. II. Rate of Polymerization

BY F. O. RICE AND JOSEPH GREENBERG

The tendency of gaseous ketene to condense to a brown liquid on standing has been referred to by Wilsmore in his original paper[1] on this compound. However, by working quickly he was able to manipulate the substance in the gaseous state and conduct analyses by exploding a measured volume with an excess of oxygen. In the liquid state, on the other hand, the change occurred very rapidly at room temperature and, though more slowly,[2] even at $-30°$. The product formed was found to consist mainly of cyclobutadione-1,3.

We decided to investigate the polymerization of ketene in the gaseous and liquid states, and in solution, with a view to determining the mechanism of the condensation.

There does not seem to be any appreciable homogeneous polymerization of the ketene in the gas phase. When ketene gas is introduced into a clean Pyrex vessel over mercury, there is usually no decrease in volume for an hour or two. Suddenly one or more brown spots of polymerized ketene appear and condensation at these points occurs rapidly. However, this behavior is very erratic, and while some samples of ketene could be preserved at room temperature for several days, other samples were polymerized completely during the course of an hour or two. We tried several experiments in which we cleaned the containing vessel very carefully with chromic acid and fire polished the surface, but the same erratic behavior occurred. To determine whether this behavior was connected with the presence of mercury we sealed up ketene in a clean flask and kept it at room temperature in the gaseous state at approximately atmospheric pressure. After twenty-four hours brown spots began to appear on the walls and in the course of the day the ketene had largely polymerized. A repetition of this experiment gave the same result.

Liquid Ketene.—If made without special precautions liquid ketene polymerizes appreciably at $-80°$; however, when distilled free from particles of carbon, fragments of rubber or traces of resinous material and kept in a Pyrex vessel, it is fairly stable. An average of three determinations made by weighing the residual polymer formed from a known weight of ketene kept at $-80°$ showed that only 0.8% of the original material had polymerized in one week.

If liquid ketene is sealed up in a tube and allowed to warm at 0° it polymerizes completely in an hour and a half; this was determined by placing the tube in an ice calorimeter and noting how long heat was given out.

Ketene in Solution.—Before the rate of polymerization of ketene in solution could be studied it was necessary to devise a method of estimating the concentration of ketene in the various solvents. Titration with standard alkali is not satisfactory because the polymer interferes with the end-point. Finally we used a modification of a method for analysis of acetic anhydride which has been investigated by Whitford.[3] Our apparatus consisted of a Pyrex bulb of approximately 20-cc. capacity fitted with a small dropping funnel and connected by means of capillary tubing with a graduated gas buret. A small quantity of a saturated solution of anhydrous oxalic acid in acetone is first introduced into the bulb through a stoppered side arm. A measured amount of the ketene solution is then run in from a pipet, the side arm is closed and the bulb is placed in a small thermostat at room temperature and shaken; a drop of pyridine is introduced from the dropping funnel and when the reaction is complete (after about ten minutes) the volume of carbon monoxide and carbon dioxide can be measured. It is of course necessary to apply a correction for the vapor pressure of the solvent in the bulb. When the ketene solution is transferred by means of a pipet there is a small loss of ketene, which accounts for the fact that the results are usually 2–3% too low.

The rate of polymerization of ketene in the different solvents was studied in a 50-cc. long-necked glass-stoppered Pyrex flask. This was placed in crushed ice contained in a Dewar flask. The solvent was first saturated with carbon monoxide and carbon dioxide and then placed in the flask; after fifteen minutes or more 1–2.5 cc. of liquid ketene was bubbled into it. A small sample of the solution was immediately withdrawn with a pipet and analyzed according to the above method. Other samples were withdrawn at measured time intervals. All the solvents were dried with calcium chloride and purified by distillation.

In Table I are given the complete data for the rate of polymerization in acetone as determined in a typical experiment.

TABLE I

RATE OF POLYMERIZATION OF KETENE IN ACETONE AT 0°

The concentration of ketene was determined by withdrawing 1-cc. samples at definite time intervals and the values of k_2 were obtained by substituting the concentration terms in the equation for a bimolecular reaction.

Time, min.	Concn. ketene, moles/liter	k_2
0	0.524	...
16.5	.459	0.0145
31	.409	.0173
73	.346	.0134
129	.272	.0137
181	.232	.0133
	Mean	0.0148

It will be seen that the rate of polymerization follows a bimolecular law quite closely. This statement holds also for all the other solvents in-

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[1] Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907).

[2] Chick and Wilsmore, *ibid.*, **97**, 1978 (1910).

[3] Whitford, THIS JOURNAL, **47**, 2939 (1925).

vestigated, although the rates varied very widely. This behavior, coupled with the fact that the measurements were easily reproducible, is evidence against the existence of a chain reaction. In Table II we give a summary of the results obtained using different solvents.

A suggestion that our measurements might be affected by the presence of small quantities of oxygen led us to perform some further experiments to test this point. A survey of the literature on the effect of oxygen on polymerization processes shows that the result varies greatly with the type of compound used, and sometimes even with the same compound oxygen catalyzes the formation of one polymer but not that of another. Thus, the polymerization of chloroprene[4] to the β-polymer, a volatile terpene-like substance, is not catalyzed by oxygen nor inhibited by antioxidants whereas oxygen is an extremely powerful catalyst for the formation of the plastic (α) polymer. Staudinger and Lautenschläger[5] have also recently examined the effect of oxygen on the polymerization of a number of compounds and found an acceleration in some cases and in others not. Cyclopentadiene, for example, polymerizes freely at room temperature but the rate is independent of the presence or absence of oxygen.[6] On the other hand styrol shows a strong acceleration of the rate of polymerization in the presence of oxygen.

We have found the polymerization of ketene to be entirely independent of the presence or absence of oxygen or peroxides. Pure liquid ketene through which pure oxygen was bubbled for one hour did not polymerize any more rapidly at −80° than did ketene sealed up in the absence of oxygen. Furthermore the rate of polymerization in acetone was not affected either by bubbling oxygen through the solvent before use, or by the addition of ascaridole or trimolecular acetone peroxide;[7] the rates in all cases were the same as when the experiment was conducted in the absence of oxygen.

We also examined the effect of hydroquinone[8] and anthraquinone on the rate of polymerization of ketene in acetone solution. We did these experiments very carefully and have satisfied ourselves that if these inhibitors have any effect it is very small (less than a 20% reduction).

TABLE II

RATE OF POLYMERIZATION OF KETENE IN DIFFERENT SOLVENTS AT 0°. THE VELOCITY CONSTANTS k_2 WERE CALCULATED ACCORDING TO A BIMOLECULAR LAW

Solvent	Concn. of ketene, M	$k_2 \pm 10\%$
Carbon tetrachloride	0.711	0.0000465
Xylene	.756	.000386
Bromobenzene	.770	.000473
Chlorobenzene	.802	.000563
Toluene	.910	.000644
1,2-Dichloroethylene	.742	.000750
1.4 M Acetone in carbon tetrachloride	.804	.00077
Tetrachloroethylene	.511	.000998
Heptane	.309	.00153
Carbon disulfide	.468	.00177
Ethyl trichloroacetate	.640	.00190
Benzyl chloride	.861	.00225
Benzene (24°)	.502	.00280
Acetone (−23°)	.686	.00400
1,2-Dichloroethane	.774	.00425
Ethyl benzoate	.812	.00552
Chloroform	.786	.00401
Ethyl acetate	.705	.00465
1,1,2,2-Tetrachloroethane	.876	.00939
Benzyl ether	.745	.0180
Glycol diacetate	.706	.0210
Nitrobenzene (24°)	.368	.0730
Acetone (O_2 absent)	.524	.0148
Acetone (O_2 present)	.498	.0146
Acetone + 0.01 M ascaridole	.494	.0142
Acetone + 0.014 M acetone peroxide	.513	.0156
Acetone + 0.01 M hydroquinone	.937	.0141
Acetone + 0.01 M anthraquinone	.622	.0188
Acetone + 0.03 M acetyl chloride	.572	.0168
Acetone + excess solid KCl	.765	.0159

A study of the velocity constants shows that in general the rate of polymerization is slower in solvents of low dielectric constant and that neither size of the molecule nor degree of chlorination seems to have any effect.

There seemed to be some indication that a solution of ketene in carbon tetrachloride was completely stable and that polymerization only took place above the solution. We disproved this by conducting the experiment in a vessel so arranged that no condensate which formed on the walls could run back into the solution. Under these conditions the rate of polymerization was unchanged.

The rate of polymerization of ketene in acetone was measured at 20°; k_2 was found to have a value of 0.0602; inserting this value and the value obtained at 0° (see Table II) in the Arrhenius equation gave 11,000 cal. as the activation energy of the polymerization process.

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[4] Carothers, Kirby and Collins, THIS JOURNAL, **55**, 789 (1933).

[5] Staudinger and Lautenschläger, *Ann.*, **488**, 1 (1931).

[6] See also Schultze, THIS JOURNAL, **56**, 1555 (1934)

[7] Bayer and Villiger, *Ber.*, **33**, 858 (1900).

[8] Hurd, Sweet and Thomas, THIS JOURNAL, **55**, 335 (1933), have reported that the polymerization of pure liquid ketene at −80° is retarded by a trace of hydroquinone.

Summary

We have studied the polymerization of ketene in the gaseous and liquid phases and in solution.

Ketene does not appear to polymerize appreciably in the gas phase at room temperature. Polymerization only sets in at one or more points on the surface of the vessel after the gaseous ketene has stood for several hours.

The pure liquid is stable at -80° but at 0° polymerization is rapid and is complete in about one and one-half hours.

In solution, ketene polymerizes according to a bimolecular law; within the limits of our experimental error (±20%) antioxidants such as hydroquinone do not inhibit the reaction and peroxides such as ascaridole or acetone peroxide do not accelerate it. There is a wide variation in the rate of polymerization depending on the solvent used and there seems to exist a rough parallelism between the rate and the dielectric constant of the solvent; solvents of high dielectric constant favor polymerization. The activation energy of the polymerization process in acetone is 11,000 cal.

BALTIMORE, MARYLAND RECEIVED JULY 5, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VERMONT]

The Preparation of Some Monoguanidines of Possible Physiological Significance[1]

BY CHARLES E. BRAUN AND WINIFRED M. RANDALL

Physiological studies in this Laboratory have shown that, when administered subcutaneously to normal rabbits, benzylguanidine produces a hyperglycemia followed by a marked hypoglycemia, and that β-phenylethylguanidine also exerts a hypoglycemic effect but with a less marked preliminary hyperglycemia. The latter compound, in larger doses, exerts a powerful effect upon the flow of blood as evidenced by the difficulty of bleeding the animals. The physiological effects of these compounds, together with their apparent low toxicity and the fact that they produced no observed deleterious effects upon the dosed animals, suggested the extension of these types for use in studying the relationship between guanidine structure and hypoglycemic activity.

With this in mind, the following series of new monoguanidines was prepared: γ-phenylpropylguanidine sulfate, ϑ-phenylbutylguanidine sulfate, hexahydrobenzylguanidine sulfate, β-cyclohexylethylguanidine sulfate, α,α-phenylbenzylguanidine hydrochloride, α,α-dibenzylguanidine hydrochloride, α,β,γ-tribenzylguanidine trihydrochloride and α,β,γ-tribenzylguanidine monohydrochloride.

α,γ-Dibenzylguanidine hydrochloride was synthesized by a new method involving S-methyl benzylisothiourea hydroiodide not previously described in the literature. The hydrochloride melted at 186°, which is not in agreement with 176° as reported by Strakosch who prepared it from benzylcyanamide and benzylamine hydrochloride.[2]

The reactions involved in our synthesis of α,γ-dibenzylguanidine hydrochloride establish definitely that the two benzyl radicals must be on the α and γ nitrogen atoms. This, plus the analytical data and the fact that our compound had the same characteristics, including slight water solubility ascribed by Strakosch to his compound, argues that the two are identical, and that the previously reported melting point is in error. Strakosch's compound was impure as shown by the fact that the chlorine content was low, 11.42% as compared to the calculated value of 12.86% and not 11.07% as recorded in his paper.

Experimental

S-Methyl isothiourea sulfate, m. p. 245°, was obtained as described by Arndt.[3]

γ-Phenylpropylamine, b. p. 121-124° (30-35 mm.), was prepared from β-phenylethyl bromide (Eastman) by converting it into the cyanide and reducing the latter with sodium and absolute alcohol.

ϑ-Phenylbutylamine, b. p. 142-144° (42 mm.), was obtained by converting γ-phenylpropyl alcohol into its bromide according to the method of Norris, Watt and Thomas,[4] transforming the bromide into the cyanide, and reducing the latter as described above.

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[1] Abstracted from a thesis submitted by Winifred M. Randall in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of the University of Vermont.

[2] J. Strakosch, *Ber.*, **5**, 695 (1872).

[3] F. Arndt, *ibid.*, **54**, 2236 (1921).

[4] J. Norris, M. Watt and R. Thomas, THIS JOURNAL, **38**, 1071 (1916).