[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Polymerization and Thermal Decomposition of Ketene

BY ARTHUR T. WILLIAMSON[1]

The physicochemical behavior of ketene has been an almost unexplored field of study since the discovery of this compound. Early workers[2] naturally emphasized its importance both in synthetic and theoretical organic chemistry and stimulated a large amount of research work concerned with the preparation and structural determination of its derivatives.

For several reasons it was felt that the decomposition of ketene would form an ideal problem for kinetic treatment. Prominent among these was the fact that its structure is very simple and that unambiguous reactions could reasonably be expected. Furthermore, the complete elucidation of such reactions would do much to explain in a quantitative manner the drifting "final" pressure found in the thermal decomposition of acetone,[3] a reaction which is said to take place in the following steps

$$CH_3COCH_3 \longrightarrow CH_2{=}CO + CH_4 \text{ (Unimolecular)}$$
$$CH_2{=}CO \longrightarrow CO + {}^1/_2C_2H_4 \text{ (Slow, unknown order)}$$

Experimental

Apparatus.—The reaction vessel was a cylindrical Pyrex bulb, 60 × 150 mm., connected through capillary tubing to the manometer, pumps and supply lines. Pressure was read on a quartz spiral manometer balanced against a U-type mercury gage. For ordinary evacuation a two-stage mercury pump was used with an oil pump as fore vacuum, but for gas analyses the reaction products were collected by a Sprengel pump and discharged directly into the analyzing buret.

The reaction vessel was sealed into a surrounding Pyrex bulb, the space between the two being filled with carbon dioxide. The whole was mounted in an air furnace. Any slight temperature change resulted in a corresponding pressure change in the carbon dioxide which in turn operated an external mercury thermoregulator through a connecting capillary tube. Temperatures were measured by a chromel–alumel thermocouple connected to a potentiometer circuit.

The ketene generator was modeled after that recommended by Ott and his co-workers,[4] except that Pyrex was used throughout and a 1.8 meter length of No. 36 platinum wire was used to form the reaction coil. This generator was connected to a bulb reflux condenser.

Preparation of Pure Ketene.—Pure acetone was refluxed so that its vapors passed through the red-hot platinum spiral of the generator, the resulting decomposition giving chiefly methane and ketene. This mixture passed through a series of traps, the last of which was kept at −50° to remove the last traces of acetone. The ketene was condensed at −78°. When a sufficient quantity had been collected it was allowed to boil under diminished pressure to expel dissolved methane.

Whenever ketene was needed the trap was removed until the temperature of the liquid had risen a few degrees, and it was then distilled directly into the reaction vessel.

Observations

Orientation Experiments.—The introduction of ketene to the reaction vessel between 400 and 500° invariably gave an initial rapid lowering of the total pressure followed by a slow rise. At the higher temperatures the initial drop was not so great.

The dependence of this phenomenon on pressure indicated that the initial process was a bimolecular polymerization giving diketene, $C_4H_4O_2$, and an attempt was made to determine the equilibrium constants quantitatively. This was not successful, partly because of the difficulty of separating the initial drop in pressure from the subsequent rise due to decomposition, and partly because of the action of some unknown kinetic factor. Even when the equilibrium was approached from the diketene side the interference of the decomposition process obscured the polymerization. Qualitatively, the effect of temperature was such as to indicate that the amount of diketene in equilibrium mixtures would be very small above 525°.

The Thermal Decomposition.—Above 530° the decomposition of ketene became easily measurable, but the rates did not reach a limiting low value until the reaction bulb had been poisoned by several weeks of use. The same behavior occurred when the vessel was packed with Pyrex tubing, but the final reproducible values in the two cases agreed within 3% for a four-fold increase in the surface area, so the contribution of the surface reaction must be less than 1% in the unpacked vessel.

The Reaction Products.—Muller and Peytral[5] passed ketene through a platinum tube at 1150°, removed any excess ketene by treating the effluent gas with alkali, and analyzed the gaseous mixture, obtaining the following average results.

CO	C_2H_4	CH_4	C_2H_2	H_2
63.9%	21.8	9.1	2.7	2.5

Our own analyses were at much lower temperatures and were also made at various stages of the reaction.

Carbon monoxide was determined by absorption in ammoniacal cuprous chloride, ethylene by absorption in bromine water containing some sodium bromide, and methane by combustion. There was some evidence of the presence of hydrogen, but calculations made with the com-

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[1] National Research Fellow in Chemistry.

[2] *E. g.*, Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907); *ibid.*, **93**, 946 (1908); *ibid.*, **97**, 1978 (1910); Staudinger and Klever, *Ber.*, **41**, 594 (1908).

[3] See Hinshelwood and Hutchison, *Proc. Roy. Soc.* (London), **A111**, 245 (1926); Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929); Hurd and Tallyn, THIS JOURNAL, **47**, 1427 (1925).

[4] Ott, Schroter and Packendorff, *J. prakt. Chem.*, **130**, 177 (1931).

[5] Muller and Peytral, *Compt. rend.*, **196**, 279 (1933).

bustion data indicated that it never exceeded 1%. All these analyses were made over mercury.

TABLE I

PRODUCTS OF THE REACTION

Run	Temp., °C.	Reaction, %	CO	CH_4	C_2H_4
194	530	6	66.3	30.6	3.1
195	530	6	67.4	29.4	3.2
196	535	6	67.2	30.6	2.2
197	530	7	68.8	26.1	5.1
198	535	25	65.0	28.6	6.4
199	540	25	68.8	27.5	3.7
200	540	75	65.8	30.7	0.7
203	550	100	64.2	35.1	.7

The most striking result is the high proportion of methane. Assuming that the initial process is

$$CH_2{=}CO \longrightarrow CH_2^- + CO$$

we should obtain a mixture containing 66.7% CO and 33.3% C_2H_4 after the methylene radicals had polymerized. The experiments show, however, that such a process is secondary in importance to one such as

$$CH_2^- + CH_2^- \longrightarrow CH_4 + C$$

or some similar process in which carbon or a highly unsaturated hydrocarbon is deposited. A black deposit was always formed during these runs.

Kinetics of the Reaction.—The gas analyses indicate that each molecule of ketene gives one molecule of carbon monoxide and half a molecule of methane or occasionally ethylene. This was verified experimentally by leaving the mixture in the reaction vessel for ten days at 550°.

P, initial = 142.2 mm. P, final = 220.4. $P_F/P_I = 1.55$

In all decomposition measurements the reaction was smooth and rapid until it was about 10 or 12% complete, after which it became markedly slower and continued to lose speed in a manner that defied the fitting of any rate expression to it. The following example is quite typical.

TABLE II

PRESSURE CHANGE DURING DECOMPOSITION

Run 203; temperature, 550°

Time, sec.	P, mm.	Time, sec.	P, mm.	Time, sec.	P, mm.
0	142.2	495	150.6	5,580	160.4
54	143.3	597	151.9	7,500	161.0
114	144.3	780	153.2	10,200	161.9
183	145.5	951	154.4	30,900	165.8
261	146.9	1254	155.6	80,000	171.2
336	148.5	1590	156.6	864,000	219.4
414	149.7	2340	157.8	1,200,000	220.4 (complete)
		3480	159.0		

Attention was turned to the initial portions of each reaction, before the abnormal drop in velocity occurred. It was found that the dependence on initial pressure was such as to lead neither to a first or second order constant but to one exactly midway. By use of the expression $dx/dt = k[CH_2{=}CO]^{3/2}$ and the numerical results the following constants were calculated.

TABLE III

P_0	$k \times 10^7$	P_0	$k \times 10^7$
560°		550°	
55.4	326	43.0	199
74.7	338	58.5	209
91.3	339	64.4	180
111.1	332	71.8	188
121.2	317	72.4	192
130.8	334	82.8	208
174.4	312	83.6	200
202.2	308	108.7	187
		112.4	190
Mean	326	123.8	209
540°		128.6	194
62.3	123	140.8	179
67.9	132	181.4	184
76.4	134	Mean	194
83.0	126		
91.2	126	530°	
92.2	122	62.0	77.0
97.4	117	65.7	71.5
103.7	126	72.5	69.5
118.6	117	78.3	70.0
128.2	120	79.9	69.0
141.8	115	92.0	72.5
146.0	119	114.5	67.5
153.0	122	119.1	71.0
153.6	117	Mean	71.0
Mean	123		

k is given in mm. per second per mm. of ketene. On plotting the mean values in an Arrhenius curve we obtain for the energy of activation, E = 65,500 calories.

Conclusions

Three facts indicate that this reaction is of a very complex nature, namely, the adherence to a three-half order mechanism, the abnormal retardation after about 10% of the reactant has decomposed, and the formation of methane where ethylene might be expected. The first two facts can be explained on the basis of a chain reaction mechanism,[6] which under certain circumstances predicts an order of 1.5. The retardation could be caused by chain-breaking on the part of the products. The formation of methane must remain unexplained until the actual nature of the chains is determined.

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(6) See F. O. Rice, THIS JOURNAL, **56**, 284 (1934).

Summary

1. Ketene has been found to polymerize to diketene between 400 and 500°, the polymerization decreasing rapidly with increasing temperature. An attempt to find the equilibrium constants was unsuccessful.

2. Above 530° ketene has been found to decompose chiefly into carbon monoxide and methane, depositing a carbon-like mass, and yielding three molecules of gaseous reaction products for every two molecules of decomposed ketene.

3. For the first 10% of its course the decomposition is of 1.5th order, after which it loses speed and cannot be made to fit any simple kinetic expression.

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The Activation of Gases by Metals

BY LOUIS KAHLENBERG,[1] NEAL J. JOHNSON[2] AND ALFRED W. DOWNES[2]

Some time ago the former of us discovered that if various metals, even when in a high state of purity, are heated in gases like hydrogen, nitrogen, helium, argon or carbon dioxide, a very disagreeable odor is produced which is not observed under otherwise like experimental conditions when the metal is absent. This odor, while not perfectly identical in all cases, is nevertheless always very similar in nature and is perhaps best described as a burnt odor of nitrogenous character.

The present investigation was undertaken to ascertain the causes of this odor and to determine why hydrogen, when passed over hot metals, apparently acquires the ability to unite with sulfur at ordinary temperatures and to reduce ferric salts, permanganate and blue starch iodide.

Very much exceedingly careful detailed work was done on this subject which occupied almost two years. For the sake of brevity, only the essentials of the experimental methods and the results obtained will be presented.

Experimental

The metals were heated in a combustion tube 100 cm. long and 2 cm. in internal diameter. The tube was of Scotch glass. It was thoroughly cleaned and dried and hydrogen at red heat passed through it until it was perfectly odorless, before any metal was inserted. The metals were commonly heated in the tube in a scrupulously clean porcelain combustion boat. The latter was, of course, first heated empty in the tube until all traces of odor were gone before any metal was introduced. The sulfur, permanganate, ferric chloride or blue starch iodide paper was commonly placed in another clean porcelain boat in the cooled end of the tube about 5 to 10 cm. from the boat containing the hot metal. The heating was accomplished in an ordinary combustion furnace. Tubes of Pyrex glass, Jena glass, German combustion tube glass and porcelain were also employed. The results were always the same. The heating was also tried by means of electric coils instead of the gas combustion furnace. Again the results were always the same. Furthermore, heating the metals by arcing them in the gas in question also produced the same identical effects. It was thus comparatively easy to get suitable containers and methods of heating. It was also relatively easy to obtain the gases of sufficient purity. They were carefully prepared by standard methods and then passed through a series of purifying solutions and drying towers before they entered the combustion tube.

The chief experimental difficulty was encountered in the metals themselves, that is to say, in getting them of sufficient purity. By taking the very best obtainable so-called C. P. metals of standard manufacturers, or by employing metals prepared carefully here in the laboratory, it was found that all of the following gave off hydrogen sulfide when heated in pure hydrogen gas: Al, Co, Cu, Au, Fe, Mg, Ni, Pt, Ag, Pd, Sn, Zn, Cd, W, Pb, In, Si, Cb, Cr, Ta, As, Sb, Bi. Moreover, they all produced the burnt odor mentioned. These odors lasted variously from ten minutes, in the case of Pd, to eight hours in the case of Ni. The odors also varied in intensity. As long as the odor lasted the gas exhibited reducing power on permanganate, ferric salts and blue starch iodide; it also always darkened lead acetate paper, showing the presence of hydrogen sulfide. The burnt odor commonly disappeared long before the lead acetate reaction for hydrogen sulfide ceased. The presence of the latter gas showed that small amounts of sulfur were contained in all of the metals tested.

So far as the burnt odor is concerned, it was observed not only when hydrogen was employed but also when nitrogen, helium, carbon dioxide or oxygen was used. With the latter gas the odor was faint and very soon disappeared entirely. When the odoriferous gas was passed over red-hot copper oxide and then conducted into lime or baryta water a turbidity was obtained, clearly demonstrating the presence of carbon.

It was found that metals heated in a current of gas until the latter was completely odorless and then cooled and kept in that same gas or in purified air, would not again produce the odor on heating them. Neither would they

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[1] Professor of Chemistry, University of Wisconsin.

[2] Assistant in Chemistry, University of Wisconsin.