Summary

Benzylmagnesium chloride reacts with citronellal to give α-benzyl-citronellol and substance A, a glycol formed from one mole of Grignard reagent and 2 moles of aldehyde.

The structure of A has been determined and it
has been shown that the Grignard reagent does not add to the ethylenic double bond as postulated by Rupe.[1a]

A mechanism is suggested to account for the abnormal reaction of benzylmagnesium chloride during the formation of substance A.

[Contribution from the Department of Chemistry, Oregon State College]

Reaction of Acetaldehyde with Ethyl Bromide at 400°[1]

By Jack G. Roof

The kinetics of the pyrolysis of ethyl bromide has been studied extensively by Daniels and co-workers.[2] The primary step is thought to be the formation of an ethyl free radical and a bromine atom. As an independent method of checking on this primary step a series of experiments was carried out on the liberation of free radicals in ethyl bromide by the photolysis of acetaldehyde and ethyl bromide mixtures[3] at temperatures somewhat below that required to decompose the bromide at an appreciable rate. The experimental facts obtained supported the view that free ethyl radicals are formed in the thermal decomposition of ethyl bromide. In these latter experiments it was found that mixtures of acetaldehyde and ethyl bromide reacted rather rapidly in the dark at 357°, at which temperature acetaldehyde is stable and ethyl bromide decomposes at a very slow rate.

The purpose of the present paper is to describe the results of a further series of experiments on the dark reaction of these two compounds at temperatures near 400° in an apparatus better adapted to thermal reactions than was used previously for this mixture.

Experimental

Chemicals.—Acetaldehyde by Eastman Kodak Co. and ethyl bromide by Merck were used throughout. Each of these was dried over anhydrous cupric sulfate and distilled and sealed off in glass ampules under reduced pressure after the manner previously described.[3]

Apparatus.—A molten lead bath, modeled after that of Daniels,[2] was used as a thermostat. Reactions were carried out in Pyrex vessels. Pressures were measured by means of a thin glass diaphragm[4] used as a null-point instrument in an electrical circuit.

A two-liter glass reservoir, painted black to prevent any light reaction, was attached to the reaction system by means of capillary gates, designed after those of Veltman.[2a] The reservoir was evacuated to a pressure of ca. 10^{-4} mm. and warmed by a glow-coil to 60° or higher to aid in outgassing. The sealed reservoir was then cooled and bulblets of the reactants were broken in the reservoir by means

of magnetic hammers. This storage vessel was so designed that samples of gas came into contact only with glass while in storage or while being transferred to the reaction vessel. By means of magnetically-operated hammers and tractors one could open the reservoir and let a gas sample into the reaction flask. Momentary heating of two thin-walled capillary goose-necks then sealed off both reservoir and reaction flask independently. The chief advantage of the reservoir was that one could maintain constant composition of reactants while studying the other variables of temperature and pressure over a series of experiments.

A micro-analysis apparatus, essentially that of Blacet and Leighton,[5] was available for analysis of products of the last few experiments. The gaseous products passed through a stopcock and through a trap cooled in dry-ice and were collected in the analytical apparatus by means of a Toepler pump. A lower temperature in the trap would have been desirable, in order to decrease the amount of unchanged reactants being introduced into the analytical apparatus.

Results

A few preliminary experiments were carried out on the pyrolysis of pure ethyl bromide. The plots of pressure vs. time were similar to those of Daniels. There were indications of an induction period in the reaction, but the pressures used were higher than those at which this phenomenon is pronounced.[2a]

Twenty-one experiments were then performed on acetaldehyde–ethyl bromide mixtures. A summary of the data is shown in Tables I and II. Pressure–time curves for three typical runs at 404° are shown in Fig. 1. Certain facts are immediately noticeable about these plots. There was a definite induction period of comparatively long duration, with the inflection point not being reached for a matter of minutes. This induction period was quite different from the "time lag" reported for the pyrolysis of ethyl bromide. In this latter case the pressure remained constant for several minutes and then started upward at a continuously decreasing rate as required for a first-order reaction.

For the mixtures there was an abrupt drop-off in the rate of pressure increase after a certain time. This "knee" was followed by a slow pressure rise which decreased in rate over a period of another hour or more, much after the fashion of ethyl bromide alone.

(1) Published with approval of the Monographs Publications Committee, Oregon State College, Research Paper No. 78, School of Science, Department of Chemistry.

(2) (a) P. Fugassi and F. Daniels, This Journal, **60**, 771 (1938); (b) F. Daniels and P. Veltman, J. Chem. Phys., **7**, 756 (1939).

(3) J. Roof and F. Daniels, This Journal, **62**, 2912 (1940).

(4) F. Daniels, ibid., **50**, 1115 (1928).

(5) F. Blacet and P. Leighton, Ind. Eng. Chem., Anal. Ed., **3**, 266 (1931), et seq.

The rate of pressure increase for the mixture was many times as fast as that of ethyl bromide alone at the same pressure and temperature.

The higher the temperature (over the range studied, 372 to 408°) the more rapid was the rate of reaction. However, the general shape of the curve was not changed by temperature.

The first run in a "cleaned" flask[2a] was more rapid than succeeding ones made under similar conditions without introduction of air into the flask between runs. An increasingly darkening film was observed to deposit upon the walls of the flask during consecutive runs, as is the case in the ethyl bromide decomposition.

TABLE I

SUMMARY OF DATA OBTAINED

Run	Temp., °C.	$N_a{}^b$	P_0, mm.	P_b, mm.	R	t_b, min.	P_∞/P_0
1	372	0.629	132	222	1.08	15.8	1.75 (0.9 hr.)
2	373	.629	117	186	0.94	17.3	1.82 (2.5 hr.)
3	383	.629	93	151	.99	18.3	1.69 (1.0 hr.)
4	408	.562	159	251	1.03	3.0	2.01 (2.9 hr.)
5	405	.562	120	192	1.07	8.3	2.01 (6.1 hr.)
6	404	.562	99	164	1.17	9.5	..
7	407	.562	70	120	1.27	10.3	..
8	407	.562	26	a	a	a	..
9	405	.0496	72	a	a	a	..
10	405	.0496	25	a	a	a	..
11	405	.0496	37	a	a	a	..
12	404	.604	44	78	1.28	12.5	..
13	404	.604	85	143	1.13	11.0	..
14	400	.604	73	120	1.07	18.3	..
15	385	.604	56	92	1.06	35	..
16	400	.378	125	181	1.18	3.0	..
17	404	.378	103	148	1.15	3.5	..

^{a} Indicates data not observable. ^{b} N_a, mole fraction of acetaldehyde; P_0, initial pressure of mixture; P_b, pressure at "knee" in curve; P_∞, pressure at time indicated; $R = (P_b - P_0)/N_aP_0$; t_b, time at "knee" (estimated to nearest one-quarter minute).

Let P_0 designate the initial pressure, P_b the pressure at the knee in the curve, N_a the mole fraction of acetaldehyde, and t_b the time of occurrence of the knee. Define $R = (P_b - P_0)/N_aP_0$, the ratio of (the pressure increase before the break)/(the original partial pressure of the acetaldehyde). All values of R observed are given in Table I. This quantity had an average value of 1.11 ± 0.08 mean deviation. There was no consistent correlation between the value of R and the order of the runs after a flask was cleaned. Also there was no significant correlation between the observed value of R and the temperature of the reaction.

Under the same conditions of temperature and total pressure, the lower the partial pressure of acetaldehyde, the smaller the time interval until the break was reached. Also the pressure increases were less. Hence for low pressure of acetaldehyde ($N_a \sim 0.05$) the results were inconclusive. With the exception of the low pressure run 8, none of the other experiments, ranging from $N_a = 0.38$ to 0.63, offered such difficulty.

The inflection point in the rate curve was difficult to locate accurately, but it usually occurred
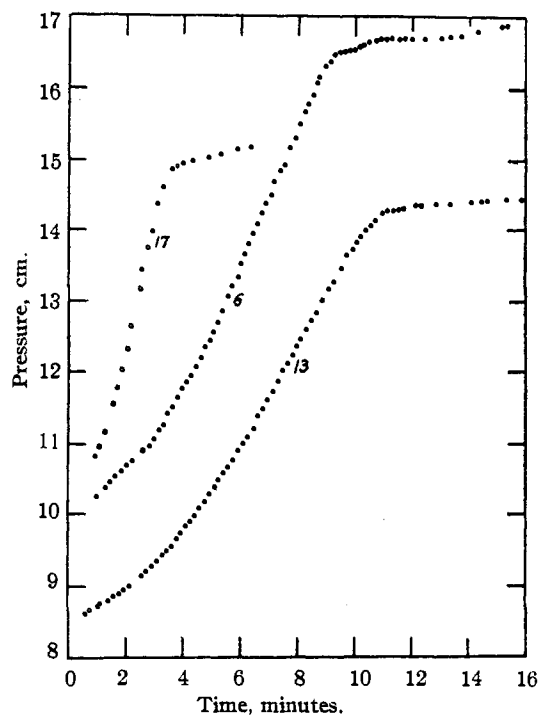

Fig. 1.—Pressure vs. time curves for three typical runs (404°): No. 17—$N_a = 0.378$; No. 6—$N_a = 0.562$; No. 13—$N_a = 0.604$.

after a pressure increase of about one-half to two-thirds of the value of $P_b - P_0$.

In the first five runs the reaction was allowed to continue for a relatively long period of time. The ratio P_∞/P_0 seemed to approach the value of 2 as a limit.

In Table II are shown results on the analysis for carbon monoxide and ethylene in the last three runs with a mole fraction of acetaldehyde of 0.378. The break time, t_b, is estimated to have been of the order of five minutes. The R values on two preceding runs on this same mixture were 1.18 and 1.15.

TABLE II

DETERMINATION OF CO AND C_2H_4 IN THE REACTION PRODUCTS

Run	Temp., °C.	Time of reaction, minutes	Ratio CO/C_2H_4
20	404	2	4.30
19	405	5	2.77
21	402	192	1.48

Discussion

The presence of both ethylene and carbon monoxide in the products and the fact that the ratio R is greater than unity indicate that the pressure increase was due to decomposition of both reactants. Although the choice of both P_0 and P_b was subject to some doubt in each experiment, the fair consistency in the values of R indicates something of the mechanism of the reaction in the early stages. From the fact that the final pres-

sure was twice the original after three to six hours, one may assume that each molecule of acetaldehyde and of ethyl bromide yielded two gaseous molecules upon reaction in the mixture; such is true for the pyrolysis of ethyl bromide[2] and the photolysis of acetaldehyde.[6] The fact that the knee occurred after a pressure increase of about 1.1 times the original partial pressure of acetaldehyde, and the fact that the CO/C_2H_4 ratio was high, would lead to the assumption that the knee indicated essential depletion of acetaldehyde in the vessel.

These interpretations would lead one to say that for a given value of R there would be $1/(R - 1)$ molecules of acetaldehyde decomposing per molecule of ethyl bromide reacting before the break. The average value of 1.11 for R would then mean the decomposition of about 9 molecules of acetaldehyde to one of the bromide. The ratio of CO/C_2H_4 should on the average be of the order of 9. Table II indicates a value of *ca.* 4. The two runs on the same mixture immediately before those analyzed gave R values of 1.18 and 1.15, suggesting a CO/C_2H_4 ratio of 5 to 7. In the previous work on this dark reaction[3] one determination of this analytical ratio was made, giving a value of 9 when N_a was 0.21 and the temperature was 355°.

If the decomposition of ethyl bromide proceeds by a chain mechanism, the chain length is short.[2a] At these temperatures acetaldehyde is itself stable, but the photolysis in the ultraviolet at temperatures above 300° occurs with quantum yields[6,7] of the order of 10^2 to 10^3. It is evident that in the present studies on mixtures the chain length of the acetaldehyde decomposition is of the magnitude of ten times that of the bromide.

The data presented herewith are considered to be in harmony with the postulated[3] decomposition of ethyl bromide into an ethyl free radical and a bromine atom, followed by reaction of the ethyl radical with CH_3CHO to form ethane, carbon monoxide and a methyl radical; this methyl radical then carries on the chain in the aldehyde decomposition. The presence of the ethyl bromide permits the acetaldehyde to decompose at this lower temperature, but it also shortens the chain length that would be possible in its absence.

(6) Mitchell and Hinshelwood, *Proc. Roy. Soc.* (London), **A159**, 32 (1937).

(7) J. A. Leermakers, THIS JOURNAL, **56**, 1537 (1934).

The induction curve obtained in this reaction is quite different from the time-lag curves obtained at low pressures of pure ethyl bromide. The "auto-catalytic" initial part of each of the present curves indicates a progressive destruction of an inhibitor or the building up of a positive catalyst until the rate begins to drop off due to the decreasing amount of aldehyde left for reaction. Since this type of curve was observed in each case and not alone in the first run in a "cleaned" flask, it is not associated with the condition of the surface of the vessel. If it is due to destruction of an inhibitor, that inhibitor must have been introduced with each new sample of the mixture into the reaction chamber. The phenomenon may be due to building up of a positive catalyst. If there is a thermal reaction of acetaldehyde and ethyl bromide together to form a complex of long life, a curve of the type obtained might be expected. If such type of activated complex is involved, it must not dissociate into ultimate molecules but must of necessity give rise to free radicals to propagate the aldehyde chain.

When conditions permit resumption of this work, it is planned to study in detail the factors influencing the induction period of this reaction.

The author is indebted to Professors Farrington Daniels and Francis E. Blacet for suggestions concerning the interpretation and presentation of these data.

Summary

1. The dark reaction of mixtures of acetaldehyde and ethyl bromide at 400° has been studied from pressure measurements and analysis of the products.

2. A pronounced induction period of an auto-catalytic type is obtained in the early stages of the reaction. A sharp decrease in the rate of pressure rise occurs after an increase of approximately 1.1 times the original partial pressure of acetaldehyde.

3 It is indicated that on the average the order of ten molecules of the aldehyde are decomposed per molecule of the bromide.

4. Correlations with previous work on the separate decomposition of these two substances is made.