

PYROLYSIS OF CHLOROMERCURYACETALDEHYDE

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Abstract. A detailed kinetic study of the pyrolysis of chloromercuriacetaldehyde (CMA) and the effect of a radical initiator (benzoyl peroxide) and a radical scavenger (hydroquinone) has been made at temperatures 217, 232 and 250°C. The rate of ketene formation follows the first order rate law. The energies of activation for the degradation of the systems CMA, CMA/BP and CMA/HQ are 12.8, 5.5 and 18.0 kcal/mole, respectively.

Chloromercuriacetaldehyde (CMA) was prepared by Nesmeyanov^{1,2} as an intermediate for a number of syntheses he carried out. Various workers used it as a starting material for the preparation of various compounds such as pure enol carboxylate^{3,4} etc. CMA was used only as a tool for synthetic organic chemistry, till recently⁵ it was pyrolysed at temperatures ranging from 217 to 250°C. It was reported that on degradation, it breaks down to give ClHg^o and °CH₂CHO radicals, ultimately yielding ketene, acetaldehyde and mercurous chloride.

On mixed pyrolysis of CMA with polyvinyl chloride (PVC) (which alone dehydrochlorinates by a free radical mechanism^{6,12}) the dehydrochlorination of PVC was retarded and the retardation effect was dependent on the concentration of CMA which indicated that CMA could be used as a stabilizer for PVC. Therefore, the detailed kinetics and mechanism of pyrolysis of CMA was considered necessary to be investigated in the present work.

Experimental

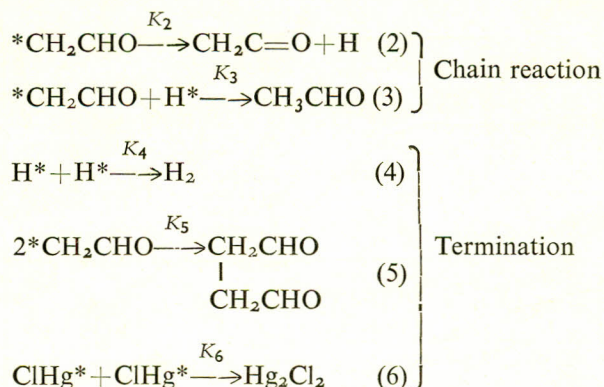
Materials. Chloromercuriacetaldehyde was prepared as described earlier.⁵ It was recrystallised in acetone. Pure needle shaped crystals had a m.p. 130°C (Lit.¹ 130°C). Benzoyl peroxide of M/s. Laporte Chemicals (Luton, England) was used. It was recrystallised in ethanol prior to be used in pyrolysis. Hydroquinone was obtained from B.D.H. (Poole, England) and was used without further purification.

Pyrolysis. Pyrolysis was carried out in a similar apparatus as described by Bengough *et al.*⁷ The exit gases were carried out with dry and oxygen free nitrogen and were bubbled into distilled water. The acetic acid produced by ketene and water were titrated with a standard N/500 sodium hydroxide solution.

Constant temperature baths were prepared by using naphthalene (b.p. 217°C), *m*-nitrotoluene (b.p. 232°C) and benzoic acid (b.p. 250°C).

Results and Discussion

On the basis of the products isolated from the pyrolysis of CMA, the following scheme for the degradation of CMA was proposed⁵.



From the reaction scheme a number of kinetic relations can be derived in terms of measurable species from the pyrolysis of CMA.

The ethenoxy radicals are produced in equation 1 and consumed in equations 2, 3 and 5. At steady state,⁸ the rate of the production of ethenoxy radicals is equal to their destruction.

$$K_1[\text{CMA}] = K_2[\text{°CH}_2\text{CHO}] + K_3[\text{°CH}_2\text{CHO}][\text{H}^*] + K_5[\text{°CH}_2\text{CHO}]^2 \quad (7)$$

If the steady state conditions are also applied to hydrogen atoms, we have

$$K_2[\text{°CH}_2\text{CHO}] = K_3[\text{°CH}_2\text{CHO}][\text{H}^*] + K_4[\text{H}^*]^2 \quad \text{or}$$

$$K_4[\text{H}^*]^2 = K_3[\text{°CH}_2\text{CHO}][\text{H}^*] - K_2[\text{°CH}_2\text{CHO}] \quad (8)$$

on adding (7) and (8):

$$K_1[\text{CMA}] = 2K_3[\text{°CH}_2\text{CHO}] + K_5[\text{°CH}_2\text{CHO}]^2 + K_4[\text{H}^*]^2 \quad (9)$$

Under the experimental conditions of the pyrolysis of CMA, the amounts of hydrogen and succindialdehyde were too small to be detected, hence the possibility of their formation could be neglected, which means, that $K_4 \approx 0$ and $K_5 \approx 0$.

Therefore, equation 9 could be simplified as:

$$[\text{°CH}_2\text{CHO}] = \frac{K_1}{2K_3} [\text{CMA}] \quad (10)$$

Similarly, a kinetic scheme for the ClHg* radicals can be derived considering that at steady state the rate of change of concentration of Hg₂Cl₂ will be zero:

$$d[\text{Hg}_2\text{Cl}_2]/dt = K_1[\text{CMA}] - K_6[\text{ClHg}^*]^2 = 0$$

$$\text{or } K_1[\text{CMA}] = K_6[\text{ClHg}^*]^2 \quad (11)$$

Equation 7 can be written as

$$K_6[\text{ClHg}^*]^2 = K_2[*\text{CH}_2\text{CHO}] + K_3[*\text{CH}_2\text{CHO}][\text{H}^*] + K_5[*\text{CH}_2\text{CHO}]^2$$

$$\text{or } [\text{ClHg}^*]^2 =$$

$$[*\text{CH}_2\text{CHO}] \left[\frac{K_2 + K_3[\text{H}^*] + K_5[*\text{CH}_2\text{CHO}]}{K_6} \right] \quad (12)$$

But from equation 10, $[\text{H}^*] = (K_1/2K_3)[\text{CMA}]$.
Substituting in we get

$$[\text{ClHg}^*]^2 =$$

$$[\text{CMA}] \frac{K_1}{2K_3} \left[\frac{K_2 + K_3[\text{H}^*] + K_5 \frac{K_1}{2K_3} [\text{CMA}]}{K_6} \right] \quad (13)$$

$$\text{or } [\text{ClHg}^*]^2 =$$

$$[\text{CMA}] (K_1/2K_3) \left[\frac{K_2 + K_3[\text{H}^*] + \frac{K_5 K_1 [\text{CMA}]}{2K_3}}{K_6} \right]$$

$$\text{or } [\text{ClHg}^*]^2 =$$

$$[\text{CMA}] \left[\frac{K_1 K_2}{2K_3 K_6} + \frac{K_1}{2K_6} [\text{H}^*] + \frac{K_5 K_1^2}{2K_3^2 K_6} \right]$$

Since $K_5 \approx 0$

$$[\text{ClHg}^*]^2 = [\text{CMA}] \left[K_1 K_2 / 2K_3 + \frac{K_1 [\text{H}^*]}{2K_6} \right] \quad (14)$$

From equation 8, since $K_4 \approx 0$

$$[\text{H}^*] = K_2 / K_3 \quad (15)$$

Substituting Equation 15 in equation (14):

$$[\text{ClHg}^*] = [\text{CMA}]^{1/2} K_1 K_2 / K_3 K_6 \quad (16)$$

The rate of formation of ketene from equation 2 can be written as

$$d[\text{CH}_2\text{C}=\text{O}]/dt = K_2[*\text{CH}_2\text{CHO}] \quad (17)$$

Substituting for ethenoxy radicals from equation 10 into equation 17 we get

$$d[\text{CH}_2\text{C}=\text{O}]/dt = (K_1 K_2 / 2K_3) [\text{CMA}] \quad (18)$$

It is evident from the equations 10 and 16 that the concentrations of ethenoxy and chloromercury radicals would be determined at any time of the reaction. The rate of production of ketene can be determined from the equation 18 according to which ketene formation should obey the first order rate law.

The results of these investigations have shown that the formation of ketene follows the first order rate

law only in the initial stage of the reaction, as is evident from the Figs. 1-3 and Table 1. The rate constant for the ketene formation, $K_1 K_2 / 2K_3$ for CMA alone and CMA mixed with 5% benzoyl peroxide (BP) with 5% hydroquinone (HQ) are given in Table 1.

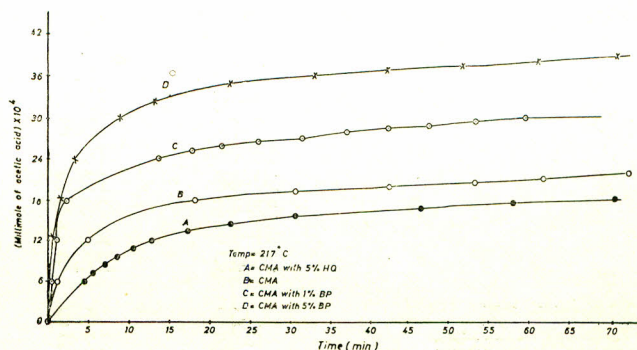


Fig. 1.

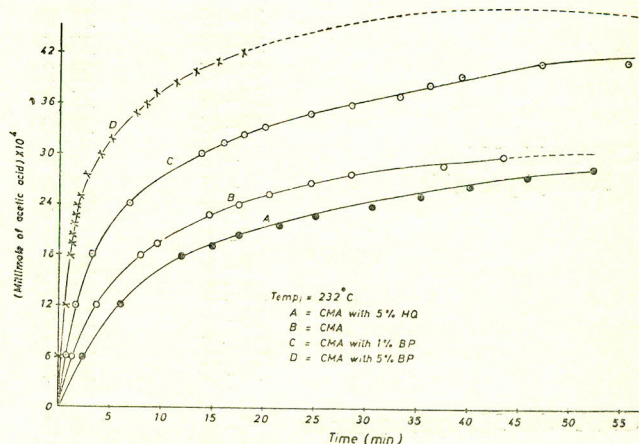


Fig. 2.

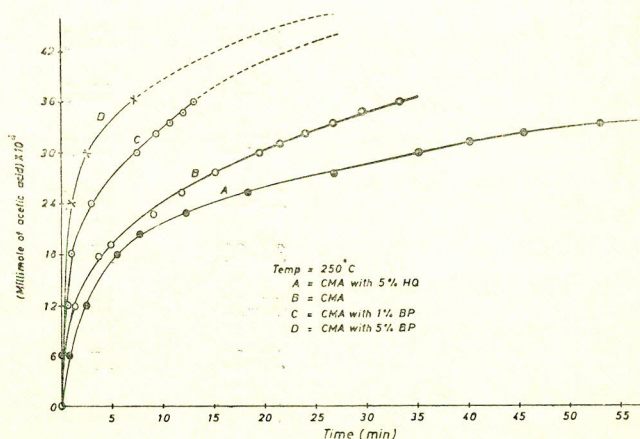


Fig. 3.

TABLE 1

System	Temperature					
	217°C		232°C		250°C	
	Time (min/sec)	Millimole of acetic acid $\times 10^4$	Time (min/sec)	Millimole of acetic acid $\times 10^4$	Time (min/sec)	Millimole of acetic acid $\times 10^4$
CMA	0-40	3.0	1-45	6.0	0-30	6.0
	1-15	6.0	4-45	12.0	1-20	12.0
	2-30	9.0	8-	18.0	4-15	18.0
	4-55	12.0	9-30	19.2	6-45	20.4
	9-50	15.0	14-30	22.8	10-15	24.0
	18-05	18.0	17-30	24.0	15-10	27.6
	30-30	19.2	31-30	25.2	19-30	30.0
	52-45	20.4	28-30	27.6	24-	32.4
	61-15	21.0	37-30	28.8	26-40	33.6
	75-20	21.6	43-30	30.0	29-15	34.8
CMA with 1% benzoyl peroxide	0-30	6.0	-45	6.0	-15	6.0
	1-05	12.0	1-45	12.0	-25	9.0
	2-10	18.0	3-20	18.0	-40	12.0
	13-30	24.0	6-45	24.0	-55	15.0
	17-45	25.2	14-20	30.0	1-05	18.0
	21-20	25.8	18-0	32.4	1-50	21.0
	25-45	26.4	20-30	33.6	3-	24.0
	31-15	27.0	28-30	36.0	7-30	30.0
	36-55	27.6	33-15	37.2	9-25	32.4
	47-05	28.2	36-15	38.4	10-45	36.6
	52-40	29.4	46-45	40.8	12-	34.8
	58-45	30.0	56-10	42.0	13-	36.0
	CMA with 5% benzoyl peroxide	-12	6.0	-20	6.0	-8
-35		12.0	-40	12.0	-20	12.0
1-45		18.0	1-20	18.0	-35	18.0
3-15		24.0	2-	24.0	-50	20.0
9-		30.0	4-	30.0	1-05	24.0
22-20		34.8	5-10	32.4	2-35	30.0
33-		36.0	8-30	36.0	4-25	32.8
51-15		37.2	9-15	37.2	6-20	34.8
70-15		38.4	11-10	39.6	7-15	36.0
CMA with 5% hydroquinone		4-	6.0	2-15	6.0	-45
	5-32	7.2	6-	12.0	2-25	12.0
	7-	8.4	11-50	18.0	5-30	18.0
	8-30	9.6				
	10-30	10.8	15-	19.2	7-45	20.4
	12-45	12.0	17-30	20.4	12-15	22.8
	17-15	13.2	21-30	21.6	18-15	25.2
	22-30	14.4	25-30	22.8	26-30	27.6
	30-30	15.6	30-30	24.0	35-15	30.0
			35-15	25.2	10-10	31.2
			40-10	26.4	45-30	32.4
	46-10	16.8	45-50	27.6	53-0	33.6
	57-30	17.4			57-15	34.2
	70-05	18.0	52-15	28.8		
			65-15	30.0	62-30	34.8

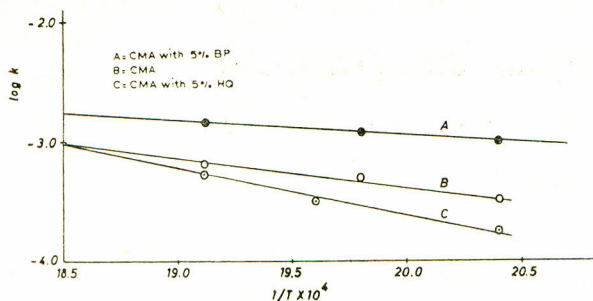


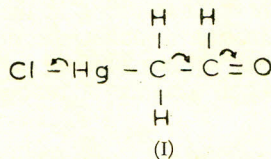
Fig. 4.

TABLE 2. THE RATE CONSTANTS FOR THE KETENE FORMATION ($K_1 K_2 / 2K_3$) $\times 10^4$.

Pyrolysis of	217°C	232°C	250°C
CMA	7.8025	12.0861	14.8705
CMA with 5% BP	23.5597	27.6143	33.2829
CMA with 5% HQ	4.1915	7.4525	12.3570

The rate of ketene formation (Table 1) are enhanced in the presence of BP and depressed in the presence of HQ which clearly indicates that ketene is found by a free radical process. It has already been suggested that ketene formation comes through ethenoxy radicals.

From the Arrhenius plots (Fig. 4) of the rate constants, the values of activation energies are 12.8, 5.5 and 18.0 kcal/mole for CMA degradation, CMA mixed with BP (5%) and CMA in the presence of HQ(5%). The rather low value of activation energy for CMA degradation is understandable if the accumulative electromeric and inductive effect on the C—Hg bond, in the linear structure (I) of CMA, is considered; in addition to the fact that C—Hg bond is very weak.⁹



The activation energies in a homolytic scission are lowered in the presence of a free radical initiator and enhanced in the presence of a free radical scavenger. The results of these investigations are in agreement with this generalization.^{10,11}

Since the rate of ketene formation on CMA degradation, is retarded in the presence of HQ, best results can be obtained if CMA, which retards the degradation of PVC,¹² is used with a low percentage of HQ in the stabilization of PVC.

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