

HYDROGEN CHLORIDE ACCELERATED DECOMPOSITION OF 2,2-AZOBISPROPANE

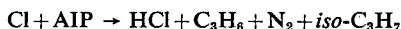
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The gas-phase pyrolysis of 2,2-azobispropane ($iso-C_3H_7-N=N-iso-C_3H_7$; AIP) was studied in the presence of hydrogen chloride at 494—546 K in a static system. The rate of decomposition of AIP was accelerated by hydrogen chloride vapour. The acceleration has been explained by the following chain reactions:



The rate constant for recombination of the *isopropyl* radical was estimated from the extent of acceleration.

Introduction

Hydrogen chloride is known to alter the rates of thermal decomposition of some organic compounds in the gas phase [1, 2]. The effect may be caused by catalysis of the transfer of hydrogen between decomposing reactant and free radicals. The result of such catalysis may be an increase in reaction rate due to catalysis of a rate-determining hydrogen-transfer step.

Measurement of the catalytic effect of hydrogen chloride has proved to be a suitable means for determination of the rate constants of some elementary reactions [3, 4]. Similarly, the pyrolysis of 2,2-azobispropane ($iso-C_3H_7-N=N-iso-C_3H_7$; AIP) in the presence of hydrogen chloride seemed to be suitable for the estimation of the rate constant of *isopropyl* radical recombination.

Experimental

The static reaction system and the analytical methods applied on the gas-chromatograph were described earlier [5, 6]. AIP was prepared by the RENAUD—LEITCH method [7] and was purified by intensive washing with water and low-temperature distillation. It was 99.8% pure, containing acetone and diethyl ether as impurities.

Hydrogen chloride vapour was prepared from the aqueous solution (Merck) by dehydration with concentrated sulphuric acid, and was dried by passage through a trap at 195 K and collected at 87 K.

Results and Discussion

The kinetics of thermal decomposition of AIP in the gas phase were reported earlier [8]. We have recently found that the rate of decomposition of this compound increases in the presence of hydrogen chloride. The acceleration can be characterized by the ratio k_{HCl}/k , where k_{HCl} and k are the rate constants of the decomposition of AIP in the presence and in the absence of hydrogen chloride, respectively. The values of k_{HCl} and k were determined from the slopes of the $\log ([\text{AIP}]_0/[\text{AIP}])$ vs. t (t =time) graphs, where $[\text{AIP}]_0$ and $[\text{AIP}]$ are the concentrations of AIP at zero time and at time t , respectively.

The extent of the acceleration depends on the concentration of hydrogen chloride. This is shown in Figure 1.

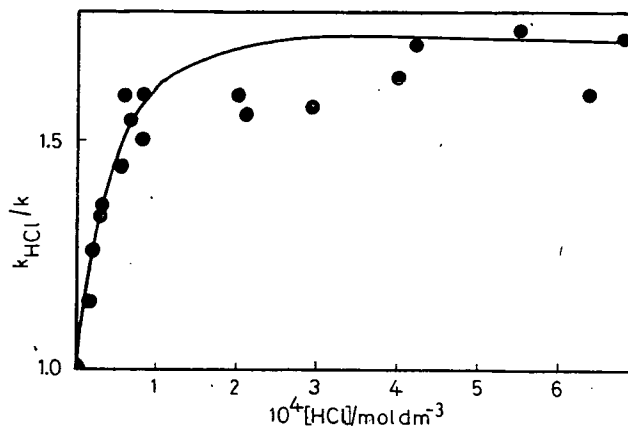


Fig. 1. The effect of HCl on the rate of decomposition of AIP

At low concentrations of hydrogen chloride the value of k_{HCl}/k is proportional to the concentration of hydrogen chloride. At higher HCl concentrations the acceleration reaches a limiting value, with k_{HCl}/k 1.7, independently of the temperature between 494 and 523 K.

The following products were identified by gas-chromatography: nitrogen, propane, propylene, 2,3-dimethylbutane (DMB) and 4-methylpentene-1 (4MP1). The products and the product composition were to be the same in the HCl-influenced (if $[\text{HCl}] < 10^{-4} \text{ mol dm}^{-3}$) and in the uninfluenced decomposition of AIP.

To explain the observations, the following mechanism can be considered:

- (i) $\text{AIP} \rightarrow 2 \text{ iso-C}_3\text{H}_7 + \text{N}_2$
- (c) $2 \text{ iso-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$ (DMB)
- (d) $2 \text{ iso-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6$
- (1) $\text{ iso-C}_3\text{H}_7 + \text{AIP} \rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6 \cdots \text{N} \cdots \text{ iso-C}_3\text{H}_7$
- (2) $\text{ iso-C}_3\text{H}_7 + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_5$ (allyl)
- (3) $\text{ iso-C}_3\text{H}_7 + \text{C}_3\text{H}_5 \rightarrow \text{C}_6\text{H}_{14}$ (4MP1)
- (4) $\text{ iso-C}_3\text{H}_7 + \text{HCl} \rightarrow \text{C}_3\text{H}_8 + \text{Cl}$
- (5) $\text{Cl} + \text{AIP} \rightarrow \text{HCl} + \text{C}_3\text{H}_6 + \text{N}_2 + \text{ iso-C}_3\text{H}_7$

By analogy with [4] the effect of HCl can be explained by reactions (4) and (5).

At higher concentrations of HCl ($>10^{-4}$ mol dm $^{-3}$) the initial rate of formation of DMB decreases, while that of 4MPI increases. This experimental observation can be interpreted as follows. Some AIP reacts in reaction (5) the products of which are N $_2$, C $_3$ H $_6$ and *iso*-C $_3$ H $_7$. In this reaction [*iso*-C $_3$ H $_7$] is lower than in the uninfluenced reaction, where most of the AIP molecules decompose to N $_2$ and 2 *iso*-C $_3$ H $_7$. (It should be noted that the role of reaction (1) in the consumption of AIP is about 10% and it is thus not too important in comparison with reaction (i) as was shown earlier [8].) The lower initial rate of formation of DMB can therefore be explained by the lower concentration of *isopropyl* radicals. The concentration of *iso*-C $_3$ H $_7$ can also be decreased by the enhanced importance of reaction (2), which is a consequence of the higher concentration of C $_3$ H $_6$ resulting from reaction (5).

As concerns the reaction at low conversion, where the main hydrogen donor is AIP, it can be concluded that the extent of acceleration is equal to the rate of reaction (5). On the basis of the mechanism, it is easy to understand that in this system the rate of reaction (5) is equal to that of reaction (4). The rate of decomposition of AIP in the presence of HCl can therefore be given by the Eqn (I):

$$R_{\text{HCl}} = R + k_4[\text{HCl}][\textit{iso}\text{-C}_3\text{H}_7] \quad (\text{I})$$

R_{HCl} and R are the initial rates of decomposition of AIP with and without HCl, respectively; k_4 is the rate constant of reaction (4). For Eqn (I) [*iso*-C $_3$ H $_7$] has been taken from the rate expression for reaction (c). From the rearranged Eqn (I) the rate constant of recombination of *iso*-C $_3$ H $_7$ can be given by Eqn (II):

$$k_c = \frac{k_4^2[\text{HCl}]^2 R_{\text{DMB}}}{[R_{\text{HCl}} - R]^2} \quad (\text{II})$$

where R_{DMB} and k_c are the initial rate of formation of DMB and the rate constant of *isopropyl* combination, respectively. Beside measurable quantities, Eqn (II) contains k_4 , which is also necessary for the estimation of k_4 . Measured values of k_4 are not available, and they were therefore calculated from the rate constant of the back reaction (k_{-4}) by thermochemical calculations. The rate constant of reaction (-4) was taken from the paper of KNOX and NELSON [9]:

$$\log(k_{-4}/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = 10.87 - (2.75 \text{ kJ mol}^{-1})/2.3 \text{ RT}$$

Thermochemical data used in the calculations were taken from the literature [10, 11] and are shown in Table I.

Table I

Thermochemical data [10,11] for *iso*-C $_3$ H $_7$ + HCl \rightarrow C $_3$ H $_8$ + Cl

	$\frac{\Delta H_{298}^0}{\text{kJ mol}^{-1}}$	$\frac{S_{298}^0}{\text{J K}^{-1}}$	$\frac{c_{p298}^0}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{c_{p400}^0}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{c_{p800}^0}{\text{J K}^{-1} \text{mol}^{-1}}$
<i>iso</i> -C $_3$ H $_7$	73.6	280.3	73.2	89.5	103.8
HCl	-92.3	186.8	29.3	29.3	29.3
C $_3$ H $_8$	103.8	269.1	73.6	94.1	113.0
Cl	120.9	165.3	21.8	22.2	22.6

The results of calculations at 494 K are as follows: $k_{-4} = 3.78 \cdot 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; equilibrium constant of reaction (4):

$$K_4 = 3.16 \cdot 10^{-6}; \quad k_4 = 1.19 \cdot 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The rate constant of isopropyl combination was calculated *via* Eqn (II). Experimental data and the results are given in Table II.

Table II
Experimental data and estimated k_c

$\frac{10^9 \cdot R_{\text{DRB}}}{\text{mol dm}^{-3} \text{ s}^{-1}}$	$\frac{10^5 [\text{HCl}]}{\text{mol dm}^{-3}}$	$\frac{k_{\text{HCl}}}{k}$	$\log(k_c/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
2.3	1.48	1.16	9.2
2.3	3.22	1.36	9.2
2.3	2.27	1.26	9.2
2.3	5.80	1.45	9.5
2.2	7.13	1.54	9.5
2.3	3.08	1.34	9.2
2.2	6.48	1.60	9.3

T = 494 K; $[\text{AIP}]_0 = 3.24 \cdot 10^{-4} \text{ mol dm}^{-3}$.

Table III
Rate constant for reaction
2 iso-C₃H₇ → DMB

$\log(k_c/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	Method	Temperature K	Reference*
9.5 ± 0.2	VLPP	683—808	[4]
9.5 ± 0.1	MMS	298	[12]
9.8 ± 0.3	MMS	301—424	[13]
9.3 ± 0.2	See text	493—523	this work

* Neglecting any temperature coefficient

VLPP = very low pressure pyrolysis

MMS = molecular modulation spectroscopy

The error in the calculation of k_4 is not included in the results shown in Table II. Taking into account the errors of estimation and measurements, the rate constant of isopropyl combination can be given by the expression:

$$k_c = 10^{9.3 \pm 1.2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

This value is comparable with rate constants of isopropyl recombination determined by other methods.

The value for k_c determined for the HCl accelerated decomposition of AIP is not in contradiction with the literature data shown in Table III. In spite of the inaccuracy in the value of k_c (owing to the high limiting error), the agreement with the literature data gives some evidence for the validity of the mechanism suggested.

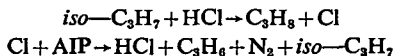
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УСКОРЕННЫЙ ХЛОРИСТЫМ ВОДОРОДОМ РАСПАД 2,2-АЗОБИСПРОПАНА

Л. Сировица

Изучен пиролиз 2,2-азобиспропана (AIP) в присутствии HCl при 494—546 К в статической системе. Скорость распада AIP увеличивался в присутствии паров HCl. Ускорение можно объяснить следующей цепной реакцией



Константа скорости рекомбинации изо-пропильных радикалов была рассчитана по ускорению реакций.