Very Low-Pressure Pyrolysis: VI. The Decomposition of Ethyl Acetate*

PETER C. BEADLE, † DAVID M. GOLDEN, and S. W. BENSON

Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025

Abstract

The pyrolysis of ethyl acetate has been studied by the very low-pressure pyrolysis (VLPP) technique. The results obtained agree well with the previously determined high-pressure Arrhenius parameters where log $k_{\infty} = 12.6 - 48.0/\theta$. The rate constants given by these parameters have also been shown to be consistent with the predictions of the RRK and RRKM theories and demonstrate the applicability of the technique to the study of thermal decompositions.

1. Introduction

The pyrolysis of ethyl acetate has been shown to be a homogeneous unimolecular reaction giving ethylene and acetic acid as its only products [1-3]. Blades and Gilderson [1] carried out the pyrolysis in a flow system using toluene as a carrier gas to eliminate any free-radical chain reactions which might occur. They measured the reaction rate by titrating the acetic acid which was formed. Scheer, Kooyman, and Sixma [2] also studied the pyrolysis in a flow system but used GLC to measure the rate of ester disappearance. However, they allowed their reactor to cool down over a series (9-14) of runs, and their results have been estimated [4] to be accurate only to within a power of 10 in the A-factor and to within 3-4 kcal/mole in the activation energy. Nevertheless, good agreement was obtained by both sets of workers, as illustrated in Table I.

$\log(A, \sec^{-1})$	E, kcal/mole	Temp., °K	Ref.
12.48	47.75	787–883	la
12.59	48.0	773-876	lb
12.04	46.5	725-810	2

TABLE I. Arrhenius parameters for the ethyl acetate pyrolysis.

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[†]Postdoctoral Research Associate.

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It was decided to study the thermal decomposition of ethyl acetate as part of a more general study of various pyrolysis reactions designed to establish the general applicability of the VLPP technique. Results have already been published for the pyrolysis of isopropyl iodide and *n*-propyl iodide [5], while those for cyclobutane are in press. Preliminary experiments [3] on the ethyl acetate pyrolysis indicate, as expected, that the observed rate constant is lower than the high-pressure value $(k/k_{\infty} \sim 0.25 \text{ at } 1020^{\circ}\text{K})$.

2. Experimental

The apparatus and experimental procedure have been described in some detail in previous papers [3,5]. A "triple aperture" quartz reactor [5] was used. This vessel has three apertures, nominally 10, 3.3, and 1 mm in diameter, which means, in effect, three reactors with collision numbers of 280, 1,920, and 22,400, respectively. The collision frequency (ω) and the escape rate constants (k_{eh}) have been calculated previously [5] and are shown below:

$$\omega$$
 (in sec⁻¹) = 4,100 (T/M)^{1/2}

Aperture Diameter (in cm)0.0970.3311.00 k_{eh} , sec⁻¹0.183(T/M)^{1/2}2.14(T/M)^{1/2}14.4(T/M)^{1/2}

Rate constants were calculated according to equation (1),

(1)
$$\frac{k_{\text{uni}}}{k_{eh}} = \frac{I_{61}^0 - I_{61}}{I_{61}} = \frac{f}{1 - f}$$

where f is the fraction of reactant decomposed.

Spectroquality ethyl acetate (Matheson, Coleman, and Bell, Norwood (Cincinnatti) Ohio, East Rutherford, New Jersey) was thoroughly degassed and fractionated under vacuum. Analysis of the acetate by mass spectrometry and gas chromatography showed no detectable impurities. Equimolar, binary mixtures of ethyl acetate with argon, acetic acid, and ethylene were used to calibrate the mass spectrometer. The ester-argon mixture was used to study the pyrolysis in the temperature range 772–1157°K.

3. Results

The reaction rate was measured by following the concentrations of the ester, olefin, and acid relative to the internal standard argon. The ethylene concentration was monitored using the 26-amu fragment peak since both the ester and the acid contributed, to a considerable extent, to the 27-amu and 28-amu peaks. Ethyl acetate and acetic acid have the same major peak (43 amu), and for this reason the ester concentration was monitored using the 61-amu fragment peak while the 60-amu parent peak was used for the acid. These peaks are both relatively minor but are still significant.

Experiments were carried out at two flow rates in the 22,400-collision reactor (see Table IV), and we can relate flow rate to the gas-gas collision frequency by using the kinetic theory. Since the gas-wall collision frequency for any particular gas varies only with temperature, we can therefore determine whether, at any flow-rate, gas–gas collisions or gas–wall collisions are more numerous. At 3×10^{15} molecules/sec, the gas-wall collisions are predominant, whereas at 2 \times 10¹⁶ molecules/sec, the gas-gas collisions should be about 8 times more frequent, and so the "effective" collision frequency at the higher flow should be $9\omega_s$. This type of increase in collision frequency should lead to an increase by a factor of 2.5 in rate constant, but no observable effect was noted (Table IV). In a series of experiments carried out in a different reactor, there was some evidence that the rate constant did increase with increasing gas pressure. However, these experiments were only qualitative and will not be discussed here, although there is evidence [6] that intramolecular gas collisions are not totally efficient in transferring internal energy. This would mean that the increase in rate constant obtained by increasing gas pressure would not be as large as the strong collision assumption would indicate.

In calculating the unimolecular rate constants, each aperture setting was treated separately, and the results are expressed in Tables II–IV. In Figure 1, the mean of the rate constants obtained from the ester, acid, and olefin concentrations is plotted against temperature for each of the aperture settings. Because of the magnification of the experimental inaccuracy inherent in eq. (1), only those runs between 10% and 90% decomposition are portrayed on the graph.

	1				
		Product			
Temp., °K	Ester decay	acid	olefin	- Average rate constant k , sec ⁻¹	
942	21.5	21.4	14.7	11.2	
941ª	23.6	21.0	12.7	11.1	
975	39.5	34.4	29.7	24.8	
1004	44.1	45.5	36.2	35.0	
1041	58.7	61.5	52.8	67.2	
1080	64.0	67.4	66.5	97.5	
1082ª	64.0	74.3	64.7	112	
1103	69.3	74.8	74.0	156	
1103ª	70.3	79.3	72.4	166	
1126	77.0	79.3	79.5	189	
1124ª	74.7	82.7	78.5	188	
1156	83.8	89.3	85.3	322	

TABLE II. Pyrolysis rate constants in the 280-collision reactor (flow rate = 3×10^{15} molecules/sec).

^a Flow rate = 2×10^{16} molecules/sec.



Figure 1. Pyrolysis of ethyl acetate.

TABLE III. Pyrolysis rate constants in the 1920-collision reactor (gas flow = 3×10^{15} molecules/sec).

]				
		Product			
Temp., °K	Ester decay	acid	olefin	Average rate constant k , sec ⁻¹	
861	13.6	10.2	14.5	0.986	
915	28.3	39.5	26.8	3.19	
941 <i>°</i>	53.2	62.5	53.8	9.13	
942	49.5	56.5	50.0	7.61	
975	69.1	72.9	64.4	15.8	
975ª	66.1	74.0	63.9	15.2	
1004	77.0	80.0	76.9	25.2	
1004ª	79.2	82.1	76.0	27.5	
1031	87.1	84.6	86.2	45.6	
1040ª	83.7	87.3	81.8	39.6	
1082	90.0	88.1	90.9	65.6	
1082ª	88.2	90.8	89.3	63.5	

^a Flow rate = 2×10^{16} molecules/sec.

	Decomposition, $\%$					
		Product				
Temp., °K	Ester decay	acid	olefin	- Average rate constant k , sec ⁻¹		
772	11.4	11.2	6.2	0.058		
787	12.7	15.3	12.6	0.085		
791ª	12.8	16.9	12.2	0.089		
807	25.8	27.3	27.0	0.201		
808ª	21.1	29.4	20.9	0.174		
830	44.6	21.7	38.2	0.347		
830ª	53.4	38.9	46.2	0.483		
915	83.3	88.3	82.8	3.28		
915ª	82.3	89.8	84.0	3.44		
943	83.0	85.8	83.0	3.11		
943ª	87.3	89.9	85.2	4.18		

TABLE IV.	Pyrolysis	rate	constants	in	the	22,400-collision	reactor	(gas	flow	=	3	Х	1015
				n	noled	cules/sec).							

^a Gas flow = 2×10^{16} molecules/sec.

4. Discussion

The percentage decompositions calculated from the ester decay and acid or olefin formation agree to within 10% in most cases, and there is no evidence for any reaction other than

 $CH_3CO_2C_2H_5 \rightarrow CH_3CO_2H + C_2H_4$

Although this agreement is poorer than we have previously obtained, it must be remembered that it was necessary to use relatively minor peaks in measurement of the ester and acid concentrations. Both of these compounds, especially the ester, contributed to the mass-spectral peak used in the ethylene determinations, and, as we would expect, the discrepancies are generally greater at low conversion.

Figure 1 illustrates the excellent agreement found between rate constants measured at different aperture settings. The values of k obtained in the 1920-collision reactor are consistently lower than those obtained in the 280-collision vessel. However, this represents only a small error in the relative escape rate constants, and we can conclude that the reactor escape rate constants are substantially correct. Consequently, the reactor dimensions and geometry are well defined.

In a recent publication [7] a comparison was made of the RRK and RRKM theories as applied to thermal unimolecular decompositions. It was concluded that, in most practical cases, both theories gave almost identical results when the approximation $s = C_{vib}/R$ is used in the RRK theory. Both theories were applied to the ethyl acetate pyrolysis and the good agreement between experiment and

theory can be seen in Figure 1. At 1000°K the VLPP rate constant is approximately 30% of the high-pressure value. The molecular parameters were those of Blades and Gilderson [1b]. The vibrational frequencies are based on the data of Dembitskii and Sumarokova [8], and the moments of inertia were calculated using normal bond angles and distances and assuming a six-centered transition state [9,10]. These molecular parameters lead to S^0 EtOAc (298°K) of 86.3 e.u. compared with 85.5 e.u. predicted by additivity and 86.7 e.u. determined experimentally [11].

	Molecule	Complex
 Frequencies (and		
degeneracies), cm^{-1}	3000 (8)	3000 (7)
c	1740 (1)	2200 (1)
	1450 (6)	1450 (5)
	1390 (1)	1400 (1)
	1280 (1)	1310 (2)
	1150 (5)	1140 (5)
	900 (3)	850 (2)
	780 (3)	710 (3)
	640 (1)	575 (1)
	400 (3)	400 (5)
	147 (2)	200 (3)
	100 (1)	
Free internal rotations	(C₂H₅∳O—)	
$10^{114} \cdot (I_{\rm A} \cdot I_{\rm B} \cdot I_{\rm C}), ({\rm g \ cm}^2)^3$	18.72	15.41
$10^{40} \cdot I_r$ (int. rot.), g cm ²	72.3	
$\sigma \div n^a$	1.0	1.0
σ_{int} (int. rotation)	3.0	1.0
Collision diameter, Å	5.	5

TABLE V. Molecular parameters for the ethyl acetate pyrolysis.

^a σ = External symmetry number; n = number of optical isomers.

5. Conclusions

The VLPP technique has been shown to give results for the pyrolysis of ethyl acetate which are in excellent agreement with the Arrhenius parameters previously determined by conventional techniques. This provides another proof of the general applicability of the technique to the study of pyrolysis reactions.

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