

CHEMICAL KINETIC MODELLING STUDIES

Part-I. The Reaction of Hydrogen Chloride with DI-Tertiary Butyl Peroxide

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The chemical kinetic modelling studies of the reaction of three torr of hydrogen chloride and one torr of di-*t*-butyl peroxide (dtBP) mixture was carried out, at 383°K, over a reaction time of 0-2500 seconds. The "Gear" programme was used to model this study. This modelling system assisted in choosing the reaction steps for a probable mechanism and in the assessment of rate parameters for individual steps in reaction mechanism.

Key words: Kinetic, Elementary rates, Modelling studies.

Introduction

In the chemistry of hydrocarbon oxidation at temperature less than about 900°K the chemistry of alkyl and alkyl peroxy plays a central role [1]. The reaction of alkyl radicals R with O₂ can lead either to RO₂, the isomerisation of which can lead to propagation and branching reactions or to an alkene + HO₂ which constitutes a termination reaction under many conditions because of the inertness of HO₂. The balance between the two paths governs the rate of products of reaction.

In this study an alkyl peroxy alkyl radical was generated by the attack of chlorine atom on di-*t*-butyl peroxide which further decomposes into olefin and oxirane. In order to refine and establish a reaction mechanism, this study was modelled because chemical kinetic modelling has become an important tool in the analysis of combustion systems.

In the recent past there have been significant development in the tools available for data analysis. Numerical integrations of different equations, which describe a reaction system, is becoming increasingly important to chemical kinetics. The theory of this model is interesting but the results which are obtained are much more important.

The essential steps of a model building process are described elsewhere [2]. The following input data were required to use the 'Gear' [3] computer programme under constant value and temperature conditions.

- i. Reaction time and step time intervals.
- ii. Concentration of each species present at the beginning of the reaction.
- iii. Reaction scheme, including all possible reaction steps in the mechanism with their associated Arrhenius parameters.

In all models, the parameters which are unknown can be estimated as:

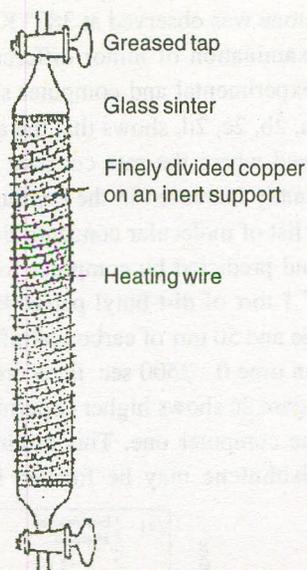
- i. By comparison of the same type of reactions.
- ii. By calculating from available information.
- iii. By choosing these which allow the model to fit the data as closely as possible.

Experimental

Di-*t*-butyl peroxide (Fluka) was purified by bulb to bulb distillation at 273°K. The resulting material contained less than 0.4% total impurity. Hydrogen chloride (Matheson) was purified by repeated freeze-pump-thaw cycles. Carbon tetrafluoride (Matheson) was subjected to several freeze-pump-thaw cycles followed by passage through a BTS catalyst of finally divided copper on an inert support (Fluka) to remove oxygen (Fig. 1). All reagents were stored at 76°K. Other compounds used for identification and calibration purposes were obtained from standard sources.

The apparatus was a standard "Pyrex" glass system, described some whereelse [4]. The concentrations of both peroxide and hydrogen chloride were in the range of 10^{-4.0}-10^{-4.5} M. The mixture was allowed to warm upto room temperature before the addition of carbon tetrafluoride (50 torr). The inert gas was added to enable efficient transfer of reactants into the reaction vessel. After mixing for at least 30 min, the reactants were expanded into the reaction vessel whose temperature was controlled to +0.5° C. At the end of each run, contents of the reaction vessel were condensed in two efficient traps at 76°K, after passing through a tube containing solid auramine to remove the hydrogen chloride [5]. Most of the carbon tetrafluoride was removed by pumping at 90°K, before the contents of the traps were distilled into a small sample tube and allowed to warm up. Analysis was carried out on a Perkin Elmer F-17 gas. A 2m column con-

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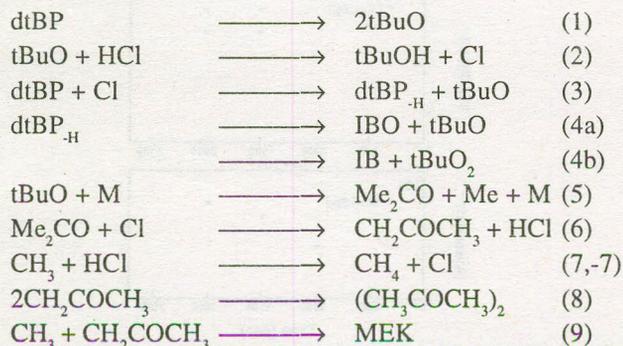

 Fig. 1. Deoxygenator for purification of CF_4 .

taining 30% dinonyl phthalate on chromosorb WAW (80-100 mesh) was used at 343°K.

Results and Discussion

A chemical kinetic reaction mechanism was used to model the pyrolysis of di-*t*-butyl peroxide (dtBP) and hydrogen chloride (HCl) system. The mechanism initially prepared to encompass all possible reaction steps, under the prescribed conditions in mechanism A.

Mechanism A



This study was carried out to determine the important reaction steps in mechanism B, to predict the results which would be obtained by experiment and to test the rate data available in the literature. Arrhenius parameters obtained from the literature [6-7] for all reaction steps in the mechanism B, are recorded in the Table 1. The differential equations used in the programme are given in Table 2.

Mechanism B

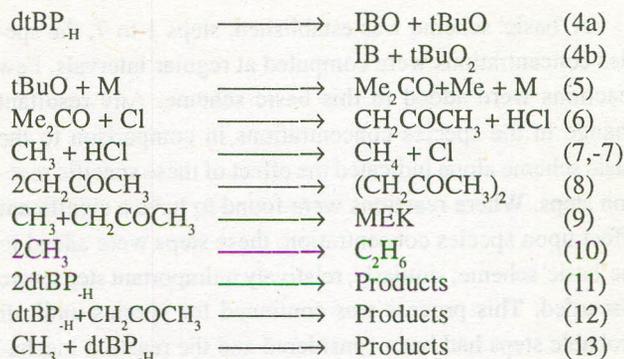
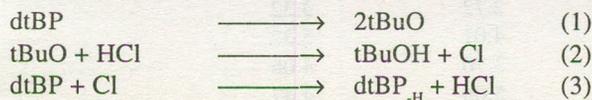


TABLE 1. RATE DATA FOR REACTIONS STEPS IN MECHANISM A AND B

Reaction No.	Arrhenius parameters		References
	log A S ⁻¹	E/Kcal mol ⁻¹	
1.	15.6	37.1	12
2.	9.0	-	13
3.	11.0	5.0	Estimated
4.(a)	12.0	14.0	5,6,10
4.(b)	13.5	20.0	5,6,10
5.	14.6	16.0	11
6.	10.5	4.5	Estimated
-7.	9.8	3.1	14
7.	8.6	1.5	14
8.	10.0	-	11
9.	10.0	-	Estimated
10.	10.0	-	Estimated
11.	10.0	-	Estimated
12.	10.0	-	Estimated

TABLE 2. DIFFERENTIAL EQUATIONS USED IN THE GEAR PROGRAM FOR DI-T-BUTYL PEROXIDE AND HYDROGEN CHLORIDE SYSTEM

$d(dtBP)/dt$	$= -k_1[dtBP] - k_3[dtBP][Cl]$
$d(IBO)/dt$	$= k_{4a}[dtBP_{\cdot H}]$
$d(IB)/dt$	$= k_{4b}[dtBP_{\cdot H}]$
$d(tBuO)/dt$	$= 2k_1[dtBP] - k_2[tBuO][HCl] + k_{4a}[dtBP_{\cdot H}] - k_5[tBuO]$
$d(HCl)/dt$	$= k_2[tBuO][HCl] + k_3[dtBP][Cl] + k_6[Me_2CO][Cl] + k_7[Me][HCl]$
$d(tBuOH)/dt$	$= k_2[tBuOH][HCl]$
$d(Cl)/dt$	$= k_2[tBuO][HCl] - k_3[dtBP][Cl] - k_6[Me_2CO][Cl] + k_7[Me][HCl]$
$d(dtBP_{\cdot H})/dt$	$= k_3[dtBP][Cl] - k_{4a}[dtBP_{\cdot H}] - K_{4b}[dtBP_{\cdot H}] - k_{11}[dtBP_{\cdot H}]^2 - k_{13}[Me][dtBP_{\cdot H}]$
$d(tBuO_2)/dt$	$= k_{4b}[dtBP_{\cdot H}]$
$d(Me_2CO)/dt$	$= k_5[tBuO] - k_6[Me][HCl] - k_{10}[Me]^2 - k_{13}[Me][dtBP_{\cdot H}] - k_9[Me][CH_2COCH_3]$
$d(Me)/dt$	$= k_5[tBuO] - k_6[Me][HCl] - k_{10}[Me]^2 - k_{13}[Me][dtBP_{\cdot H}] - k_9[Me][CH_2COCH_3]$
$d(CH_2COCH_3)/dt$	$= k_6[Me_2CO][Cl] - 2k_8[CH_2COCH_3]^2 - k_{12}[dtBP_{\cdot H}][CH_2COCH_3] - k_9[Me][CH_2COCH_3]$
$d(CH_2COCH_3)_2/dt$	$= k_8[CH_2COCH_3]^2$
$d(CH_4)/dt$	$= k_7[Me][HCl]$
$d(MEK)/dt$	$= k_9[Me][CH_2COCH_3]$
$d(C_2H_6)/dt$	$= k_{10}[Me]^2$

A 'basic' scheme was established, steps 1 to 7, the species concentrations were computed at regular intervals. Few reactions were added in this basic scheme. Any resultant change in the species concentrations in comparison to the basic scheme alone indicated the effect of these specific reaction steps. Where reactions were found to have a significant effect upon species concentration, these steps were added to the 'basic' scheme; similarly, relatively unimportant steps were discarded. This process was continued for species until all probable steps had been considered and the reaction mechanism established.

Having determined the important reaction steps, attention was concentrated upon refinement of the rate data recorded in the Table 1, with the provision that a little adjustment, as possible, was made to the rate parameters in order to predict experimental observations. Step-7, when considered due to its sensitivity, raised all the concentrations of the reactants and products which mean that step-3 was too fast. By decreasing its rate constant from 10^8 to $10^{7.3}$, this reaction becomes slow. Steps 10,11,12,13 were also considered. It was observed that these reactions were slower than steps 8 and 9 so they were discarded, except step 9.

The steps which were found to have a significant effect upon species concentration are the same as in mechanism A.

The mechanism shows that two paths are open for the decomposition of $R_{-H}OOH$, the situation is not exactly the same for $R_{-H}OOR$ radical. This is because the $RO-OH$ bond strength is some 20 KJ mol⁻¹ stronger than that in $RO-OR$ [8-10].

Arrhenius parameters for these reactions which provided the closest agreement with the experimental results are listed in Table 1.

Computer modelling of di-t-butyl peroxide decomposition involving the steps 1-9 and associated Arrhenius parameters closely predict concentrations of all species determined by experiment. Fig 2a, 2b, 2c, 2d compare the experimental concentration data with those predicted by computer for the species di-t-butyl peroxide, isobutylene oxide, isobutene, t-butanol whereas Fig. 2e, shows only the computer data for acetone concentration because experimentally

no acetone was observed at 383° K.

Examination of minor differences between the results from experimental and computer simulation, as depicted in Fig. 2a, 2b, 2c, 2d, shows that the agreement may be further improved where the rate constant for certain reactions are fractionally increased in the computer evaluation.

A list of molecular concentrations observed experimentally and predicted by computer for a typical reaction mixture of 1 torr of di-t-butyl peroxide and 3 torr of hydrogen chloride and 50 torr of carbon tetrafluoride, at 383° K, over a reaction time 0 - 2500 sec. is recorded in Tables 3-4.

Figure 2c shows higher experimental value of isobutene than the computer one. This might be due to the fact that some isobutene may be formed heterogeneously and in

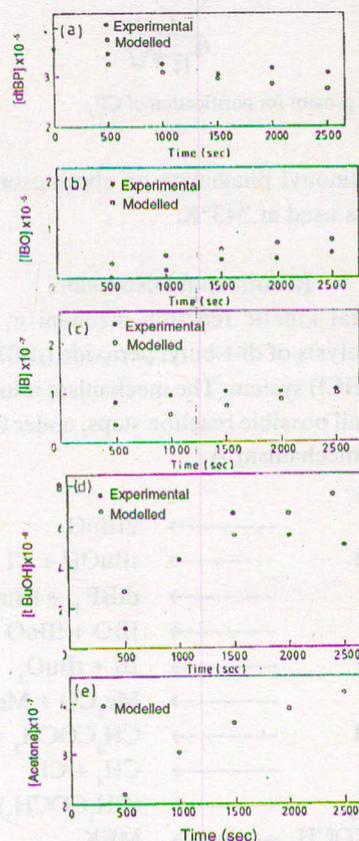


Fig. 2. Comparison of experimental data with kinetic model at 383K (a) di-t-butyl peroxide (b) Isobutylene, (c) Isobutene, (d) t-butanol, (e) Acetone.

TABLE 3. EXPERIMENTALLY OBSERVED PRODUCTS CONCENTRATION.

Temp. K	Run time (Sec)	Concentration of (M)					Me ₂ CO
		dtBP/10 ⁻⁵	dtBP/10 ⁻⁵	IB/10 ⁻⁷	IBO/10 ⁻⁶	tBuOH/10 ⁻⁶	
383	500	3.55	3.47	0.813	0.742	0.902	-
383	1000	3.55	3.25	0.924	2.72	3.32	-
383	1500	3.55	3.02	1.012	4.01	5.32	-
383	2000	3.55	3.17	0.988	3.70	4.06	-
383	2500	3.55	3.08	1.02	5.06	4.47	-

TABLE 4. COMPUTER PREDICTED PRODUCTS CONCENTRATION.

Temp. K	Run time Sec	Concentration of (M)					
		dtBP/10 ⁻⁵	dtBP/10 ⁻⁵	IB/10 ⁻⁷	IBO/10 ⁻⁶	tBuOH/10 ⁻⁷	Me ₂ CO
383	500	3.55	3.24	3.73	3.03	2.85	2.20
383	1000	3.55	3.08	5.69	4.63	4.38	3.05
383	1500	3.55	2.95	7.22	5.87	5.58	3.57
383	2000	3.55	2.84	8.50	6.91	6.60	3.93
383	2500	3.55	2.74	9.62	7.82	7.50	4.19

Fig. 2e, there is no experimental data for acetone because of separation problem of the column, G.L.C. did not resolve the acetone and isobutylene oxide peaks.

Conclusion

The modelling studies of the said reaction correctly and satisfactorily accounts for the decomposition of di-t-butyl peroxide. The hydrogen chloride was used only as a catalyst to generate the alkyl peroxy alkyl radical. The proposed mechanism can be established for such modelling studies. This also gives some kinetic data for certain steps, which was not available in the literature but estimated.

Additional information was obtained concerning the concentration of radical species in the system and also of the part played by other species in the reaction system which were not observed experimentally i.e. acetone (very very small).

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