

## CONVERSION OF 3-CARENE, $\alpha$ -PINENE, $\beta$ -PINENE AND CAMPHENE OVER PLATINUM-ALUMINA CATALYST: INFLUENCE OF CAESIUM AND FLUORIDE IONS

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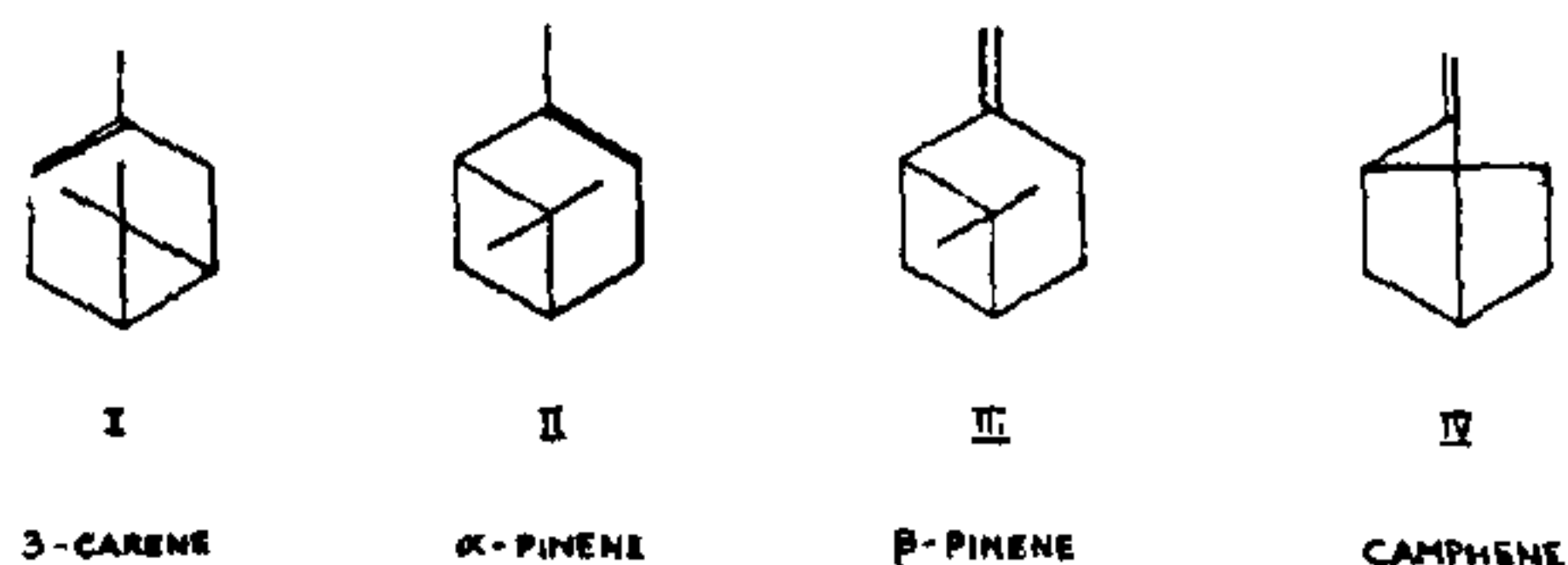
### ABSTRACT

The reactions of 3-carene,  $\alpha$ -pinene,  $\beta$ -pinene and camphene to cymenes over platinum-alumina catalyst modified with caesium and fluoride ions were studied in the vapour phase at 300° C and at a contact time of 0.79 hr. The Cs<sup>+</sup> and F<sup>-</sup> ions do not affect the overall conversion of 3-carene and pinenes to any significant extent. However, the overall conversion of camphene decreases by the addition of caesium ions and increases by the addition of fluoride ions. The fall in the dehydrogenation and disproportionation activity with increasing additions of caesium and fluoride ions is attributed to the decrease in active sites due to blocking by these ions.

### INTRODUCTION

CARENE and pinenes are found in essential oils derived from coniferae<sup>1</sup>, whose proportions vary from species to species. Indian turpentine from *Pinus longifolia* contains 3-carene (50%, b.p. 170° C),  $\alpha$ -pinene (40%, b.p. 156° C) and  $\beta$ -pinene (10%, b.p. 165° C). These bicyclic terpene hydrocarbons undergo initial isomerisation followed by dehydrogenation and disproportionation over dual function catalysts such as chromia and chromia-alumina catalysts<sup>2-5</sup>.

Platinum-alumina, another important bifunctional catalyst, is increasingly employed in reforming reactions<sup>6</sup> as it is found to possess enhanced and sustained activity with high selectivity at relatively low temperature regions. The reactivity and selectivity of the catalysts improve further by doping them with alkali and halide ions. The influence of caesium and fluoride ions on the overall conversion of 3-carene,  $\alpha$ -pinene,  $\beta$ -pinene and camphene (I-IV) as well as on the rate of formation of products has been investigated and the results are presented in this paper.



### EXPERIMENTAL

3-Carene and  $\alpha$ -pinene were from Indian turpentine, and  $\beta$ -pinene and camphene were from M/s. Fluka and more than 99% pure by gas chromatographic analysis.

Alumina was prepared from aluminium isopropoxide according to the method described earlier<sup>7</sup>. Platinum-alumina (Catalyst A) was prepared by adding calculated volume of chloroplatinic acid to a weighed amount of alumina to give 0.6% by weight (confirmed by spectrophotometric analysis<sup>8</sup>). The slurry was stirred for 3 hr and dried at 120° C for 24 hr. The catalyst was activated by maintaining the temperature at 500° C for 8 hr and was then powdered and sieved to 180-200 mesh particle size. Catalysts B, C and D were obtained by modifying catalyst A with appropriate volumes of caesium nitrate solution to give respectively 0.5, 1 and 1.5% by weight of caesium as Cs<sub>2</sub>O. Catalysts E and F were prepared by impregnating catalyst A with requisite volumes of hydrofluoric acid (40% E. Merck) to give respectively 5 and 10% by weight of HF. The above catalysts were activated, powdered and pelletised to 4 × 4 mm size pellets.

The reactions were carried out according to the method described elsewhere<sup>9</sup>. Prior to each run, the catalyst was reactivated by heating for 8 hr in a current of dry air at 500° C. The reactant liquid was fed into the reactor by a constant feed infusion pump that could displace 10 ml of the liquid/hr. The liquid products collected for the first 15 min of each run (which normally covers an hour) were discarded. The products were then analysed using an AIMIL gas chromatograph consisting of a column (1 metre) of carbowax on chromosorb.

The percentage yield of cymenes from carene and pinenes determined at different time intervals after attaining steady-state condition, showed that it did not vary significantly over a period of 2 hr thus indicating constant activity of the catalyst.

## RESULTS AND DISCUSSION

The various compounds identified in this investigation are  $\alpha$ -pinene (from  $\beta$ -pinene), dipentene, terpinolene, sylvestrene,  $\alpha$ - and  $\gamma$ -terpinenes, camphene, tricyclene, bornylene, 1-, 3- and 4(8)-*p*-menthenes, and *cis*-, and *trans*-menthanes, the major products being *p*-, and *m*-cymenes. The concentration of individual menthadienes, menthenes and menthanes was too small and they were grouped together as menthadienes and menthenes-menthanes.

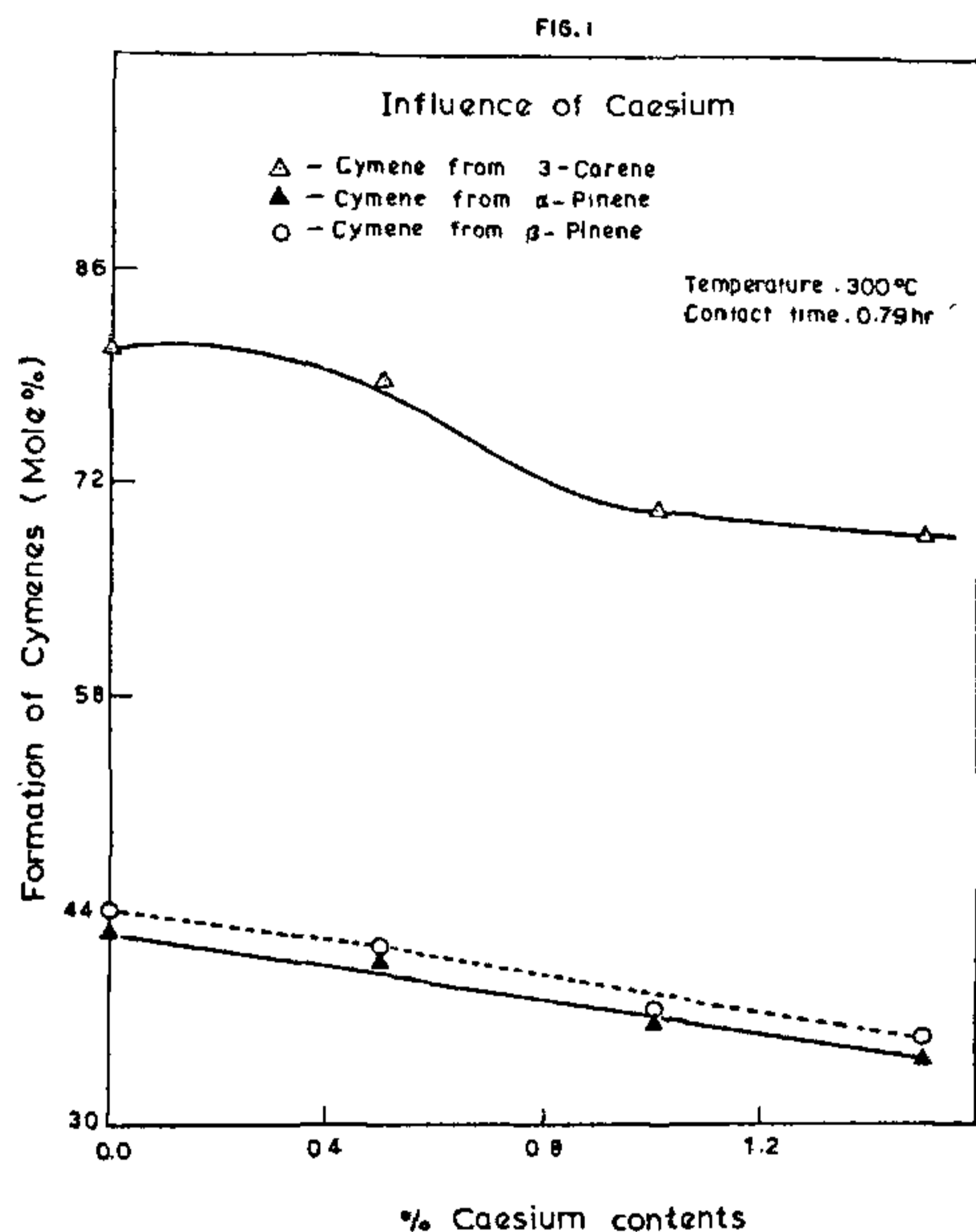


Figure 1. Influence of Caesium on the formation of cymenes.

The overall conversion of 3-carene,  $\alpha$ -pinene,  $\beta$ -pinene and camphene and the distribution of products from camphene are given in table 1. The formation of menthadienes, menthenes and menthanes is presented in table 2. The yield of bi-, and tricyclic intermediates from  $\alpha$ - and  $\beta$ -pinenes is indicated in table 3. The influence of caesium and fluoride ions on the variation of cymene yield is illustrated in figures 1 and 2 respectively.

Addition of caesium brings about a small decrease in the overall conversion of 3-carene and pinenes while a comparatively large decrease is observed in camphene (table 1). However, impregnation of the catalyst with hydrofluoric acid does not affect the overall conversion of carene and pinenes while it

enhances the overall conversion of camphene significantly (table 1).

The proportion of menthadienes is always higher from 3-carene than from pinenes (table 2). The lower concentration of menthadienes from pinenes indicates that the formation of menthadienes from bi-, and tri-cyclic intermediates is negligible. This is evident from the non-formation of menthadienes from camphene (table 1). The proportions of menthadienes in the products steadily increase with increasing amounts of caesium ions whereas with hydrofluoric acid a steep increase is observed (table 2).

The increasing concentration of menthadienes with increasing additions of both caesium and fluoride ions is attributed to a decrease in the active metal surface due to blocking by these ions. As a result, the dehydrogenation and disproportionation activity of the catalysts decreases.

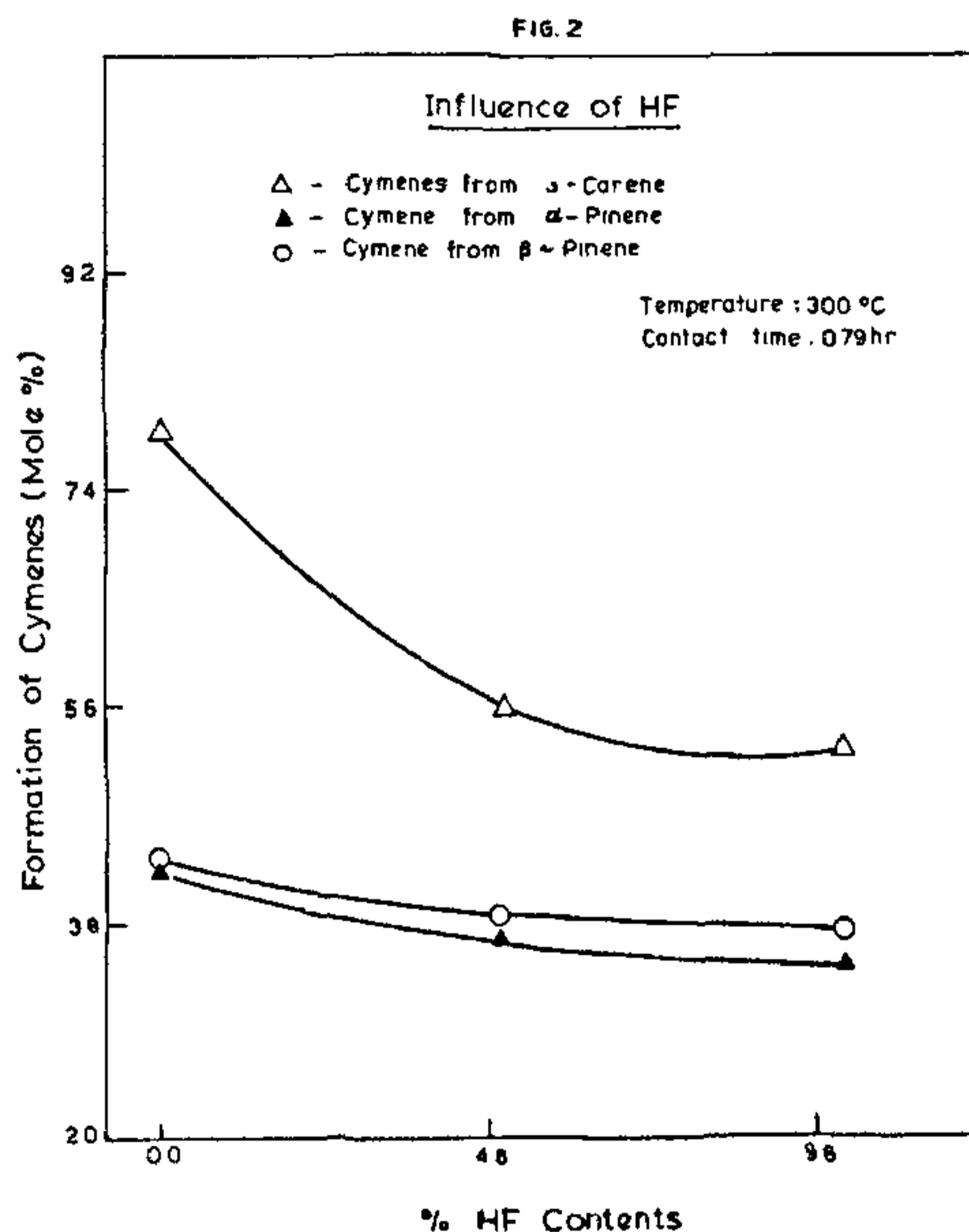


Figure 2. Influence of HF on the formation of cymenes

Caesium ions increase the formation of bi-, and tri-cyclic intermediates from pinenes (table 3) while fluoride ions decrease their formation. A sizable amount of  $\alpha$ -pinene is formed from  $\beta$ -pinene whose concentration was unaffected either by caesium or by fluoride ions (table 3). The proportions of menthanes, menthenes (table 3) and cymenes (figures 1 and 2) decrease with the addition of both caesium and fluoride ions.



TABLE 1

Overall conversion of reactants and formation of products from camphene: Effect of  $Cs^+$  and  $F^-$  ions.  
(Temperature: 300° C; Contact time\*: 0.79 hr)

Catalyst	Overall conversion of reactants (mole %)				Products from camphene (mole %)		
	3-Carene	$\alpha$ -Pinene	$\beta$ -Pinene	Camphene	Tricyclene	Bornylene	<i>p</i> -Cymene
A	96.0	82.9	99.8	65.5	58.0	5.5	2.0
B	94.0	80.9	96.0	56.6	49.4	5.2	1.1
C	93.0	79.9	95.5	55.3	49.4	4.9	1.1
D	93.0	78.0	95.8	54.8	50.0	3.8	1.2
E	93.2	83.1	98.5	70.7	60.9	6.6	3.0
F	94.5	84.2	98.8	80.5	65.7	6.8	8.0

\* Calculated on the basis of  $W/F$  ratio where  $W$  = weight of the catalyst and  $F$  = weight rate of reactant per hour.

TABLE 2

Formation of menthadienes, menthenes and menthanes from 3-carene,  $\alpha$ -pinene and  $\beta$ -pinene: Effect of  $Cs^+$  and  $F^-$  ions. (Temperature: 300° C; Contact time: 0.79 hr)

Catalyst	Menthadienes (mole %)			Menthenes and menthanes (mole %)		
	From 3-Carene	From $\alpha$ -Pinene	From $\beta$ -Pinene	From 3-Carene	From $\alpha$ -Pinene	From $\beta$ -Pinene
A	1.0	1.5	1.8	15	8.8	7.8
B	10.0	1.0	1.1	10	7.1	7.1
C	15.0	1.0	2.0	8	3.6	2.1
D	18.0	4.1	4.0	6	2.2	1.8
E	31.2	4.6	4.6	6	5.8	5.5
F	37.0	7.5	9.5	5	4.8	3.1

TABLE 3

Formation of bi-, and tri-cyclic compounds from  $\alpha$ -, and  $\beta$ -pinenes, mole %: Effect of  $Cs^+$  and  $F^-$  ions  
(Temperature: 300° C; Contact time: 0.79 hr)

Catalyst	From $\alpha$ -Pinene*			From $\beta$ -Pinene			
	Camphene	Tricyclene	Bornylene	Camphene	Tricyclene	Bornylene	$\alpha$ -Pinene
A	12.2	13.6	4.1	16.4	12.0	4.8	10.0
B	15.1	13.0	3.8	18.5	14.3	4.2	10.8
C	21.7	13.4	3.1	22.8	16.1	3.6	10.9
D	22.7	13.1	2.4	23.8	16.6	3.0	10.6
E	10.9	21.1	3.2	16.4	19.0	3.6	10.0
F	10.7	23.6	3.1	12.0	23.4	2.0	10.8

\* No  $\beta$ -pinene was detected in the product.

## CONCLUSION

Para- and meta-cymenes, which are the major products of this investigation, are of great industrial importance with respect to their oxidation products. Terephthalic acid, the oxidation product of *p*-cymene, is an important raw material for the manufacture of synthetic polyester fibres, while iso-phthalic acid, the oxidation product of *m*-cymene is an additive in plastics as heat and fire resistant component.

## ACKNOWLEDGEMENT

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## ANTI-GONADOTROPHIC EFFECT OF DIETHYL CARBAMAZINE CITRATE IN ALBINO RATS

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## ABSTRACT

Diethyl carbamazine citrate administration to the castrated partner of the parabionts for 10 days markedly blocked the ovarian hypertrophy in the intact partner. The ovaries of intact partner remained immature morphologically as well as histologically. Similar effects were observed in the unilaterally ovariectomized adult cycling rats following treatment with the drug. These experimental findings show that diethyl carbamazine citrate acts as a antigonadotrophic agent in the albino rats.

## INTRODUCTION

SOME of the piperazines exhibit varying degree of antifertility effects<sup>1</sup>. Diethyl carbamazine citrate (DEC), commonly used in the treatment of filariasis and some forms of helminthiasis, exhibited contraceptive effects in albino rats<sup>2</sup>. The present study deals with the effect of DEC on the physiological phenomenon of ovarian compensatory hypertrophy in unilaterally ovariectomized adult rats as well as in immature parabionts.

## MATERIALS AND METHODS

Inbred Wistar strain rats used in the present study were maintained under controlled light (12 hr light:

12 hr dark) and constant temperature ( $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ) and fed with standard pellet diet of Hindustan Lever. Tap water was available *ad libitum* throughout the experimental period. The drug and vehicle were administered between 12.00 and 13.00 hr. DEC was dissolved in water and administered at a dose of 0.1 ml per rat.

Healthy adult 4-day cycling virgin female albino rats weighing 175–180 g in diestrus state were selected and divided into 3 groups, each consisting of 10 animals. Unilateral ovariectomy was performed by the standard technique. DEC was given orally from the day of operation at a dose of 20 or 40 mg/kg body weight. The surgically removed ovaries were individually weighed. The vaginal smears were taken daily during the treatment. After 14 days the rats were sacrificed by