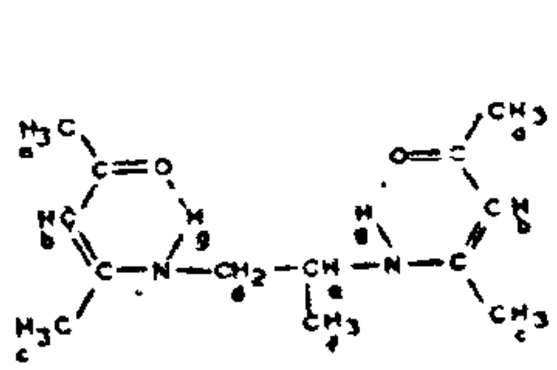
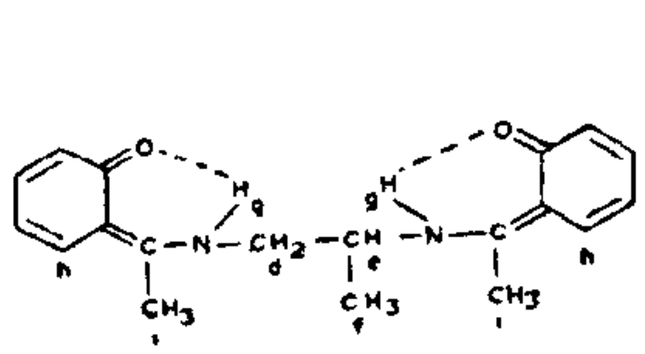


(1)



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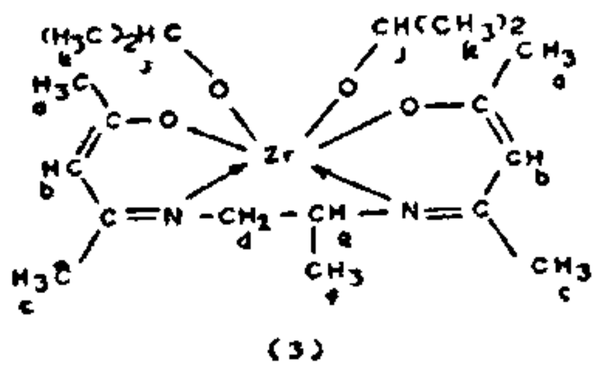

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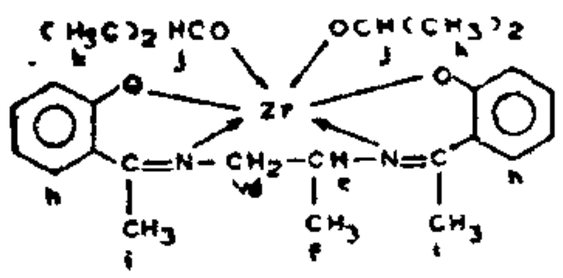

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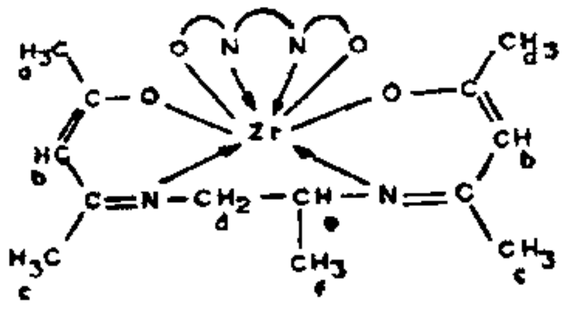

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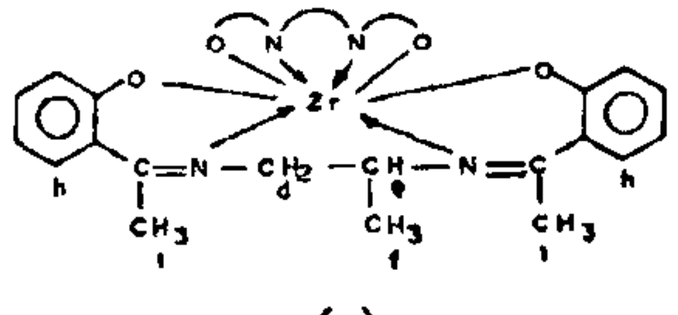

(6)

 represents the same Schiff base unit.

bases derived by the condensation of β-diketones with alkyl or arylamines or diamines as reported in the literature[1-9]. The 10·80 and 16·20 ppm peaks due to the hydrogen bonded NH protons of the ligands (1) and (2) respectively disappear in compounds (3), (4), (5) and (6) indicating their chelating nature.

In compounds (3), (4), (5) and (6), the methine, methylene and methyl proton signals are shifted downfield as compared to the ligands indicating the coordination of nitrogen of the ligand moiety to the zirconium atom.

New proton signals at 4·52, 4·50 and 1·1, 0·95 ppm in compounds (3) and (4) are due to methine and methyl protons respectively of the isopropoxy groups and which do not appear in the corresponding ligands.

ACKNOWLEDGEMENT

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MECHANISM OF UREA ADDUCT FORMATION

K. P. SHARMA, N. N. SINGH* AND K. A. KINI
Central Fuel Research Institute, Dhanbad, Bihar

ABSTRACT

The energy of activation required for penetration of $-CH_2-$group into urea lattice has been calculated by the Lennard-Jones potential energy expression method, and compared with the experimental value for the same by urea adduct experiments using dodecane at 45° and 60° C. There has been a fair agreement between the two values.

MUCH research has already been done[1] on the mechanism of separation of straight chain hydrocarbons from branch chain ones by the formation of urea adducts. It has been postulated that separation by urea adduct formation takes place by a process of penetration of the urea crystals by the hydrocarbon chains. Support has been drawn for this conclusion from x-ray studies[2] of urea adducts formed from hydrocarbons of different chain lengths.

* Present address: Department of Chemistry, Science College, Patna.

Urea crystal possesses a hexagonal lattice channel[3]. It is possible to think of a sieve action, *n*-paraffin molecules being able to pass through this structure, but not those of iso-paraffins. Potential energy, and energy of activation calculations for the penetration of xenon into hexagonal lattice channels of beryl were made by one of the authors and collaborators[4]. Values for energies of activation of the magnitude of 149 kcal/mole were obtained using the Lenard-Jones potential energy expression method[5]. It was thought that similar calculations might give a clue to the mechanism by which *n*-paraffins enter into the crystal lattice of urea. The potential energy expression, using which the values mentioned in Table I, were obtained for potential energy at different values of ring radii, is given below :

$$\phi = -A\Sigma\frac{1}{r^6} + B\Sigma\frac{1}{r^{12}}$$

$$A = \frac{6mc^6 a_C a_{CH_2}}{a_C/\chi_C + a_{CH_2}/\chi_{CH_2}}, \quad B = \frac{Ar_e\sigma}{2}$$

where ϕ = total interaction energy, m = mass of the electron, c = velocity of light, χ_C = magnetic susceptibility of carbon atom, χ_{CH_2} = magnetic susceptibility of $-CH_2-$ group, a_C = polarisability of carbon atom, a_{CH_2} = polarisability of $-CH_2-$ group and r_e = equilibrium radius of urea lattice channel. The numerical values used for the parameters[6] in the equation are :

$\chi_{CH_2} = 18{\cdot}8 \times 10^{-30}\,cm^3$,
$a_{CH_2} = 1{\cdot}83 \times 10^{-24}\,cm^3$
$\chi_C = 12{\cdot}3 \times 10^{-30}\,cm^3$, and
$a_C = 0{\cdot}96 \times 10^{-24}\,cm^3$
$r_e = 1/2$ equilibrium separation of $-CH_2-$ group + radius of oxygen atom
$= 2{\cdot}0 + 1{\cdot}4$
$= 3{\cdot}4$ Å.

TABLE I

Potential energy values for interaction between $-CH_2-$ and urea lattice channels of different radii

Radius (Å)	Potential energy (kcal/mole)
2·0	90·6
2·5	6·4
3·0	0·6
3·5	− 0·2
4·0	− 0·1
5·0	− 0·04

From the diagram showing the potential energy *vs.* radius (Fig. 1), a value of 3·3 Å for the equilibrium channel (*viz.*, the critical ring size for which the potential energy is zero)[6] was obtained. Subsequently, the potential energy of the system when a $-CH_2-$ group approaches the urea lattice channel along a line perpendicular to it, and passes through its centre, was calculated. The results are given in Fig. 2. From this, the energy of activation required for penetration (by $-CH_2-$ group) of urea crystal of the above-mentioned equilibrium ring radius was found to be 0·15 kcal/mole.

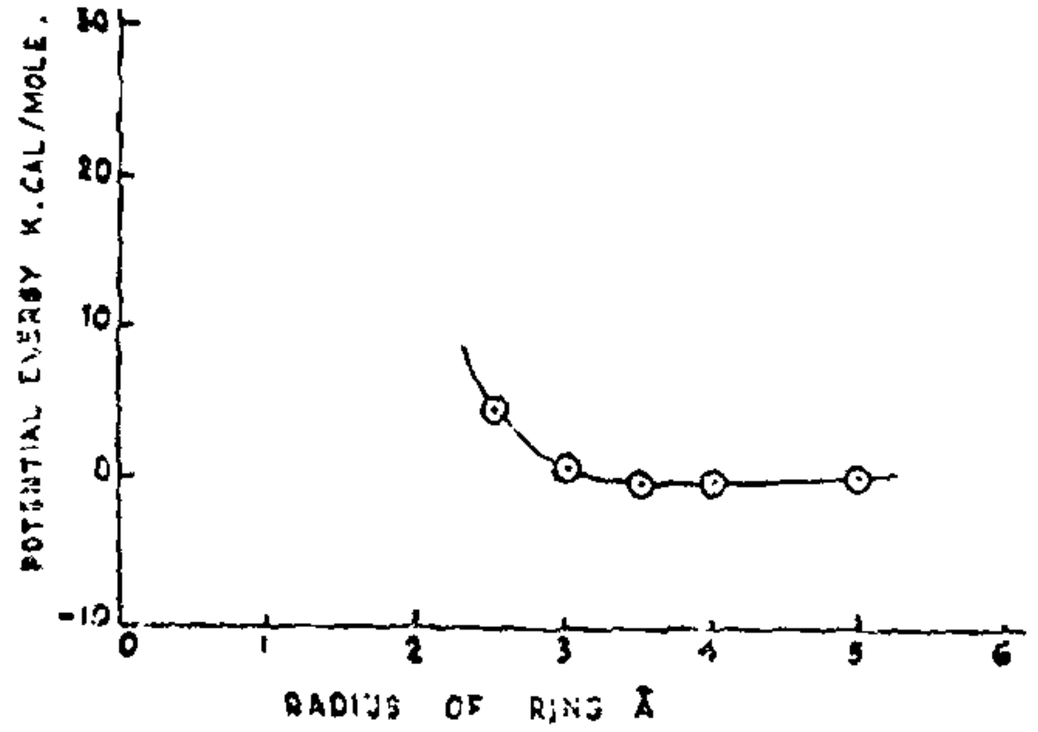

FIG. 1. Potential energy diagram for penetration of $-CH_2-$ into 6-membered urea lattice channel of different radii.

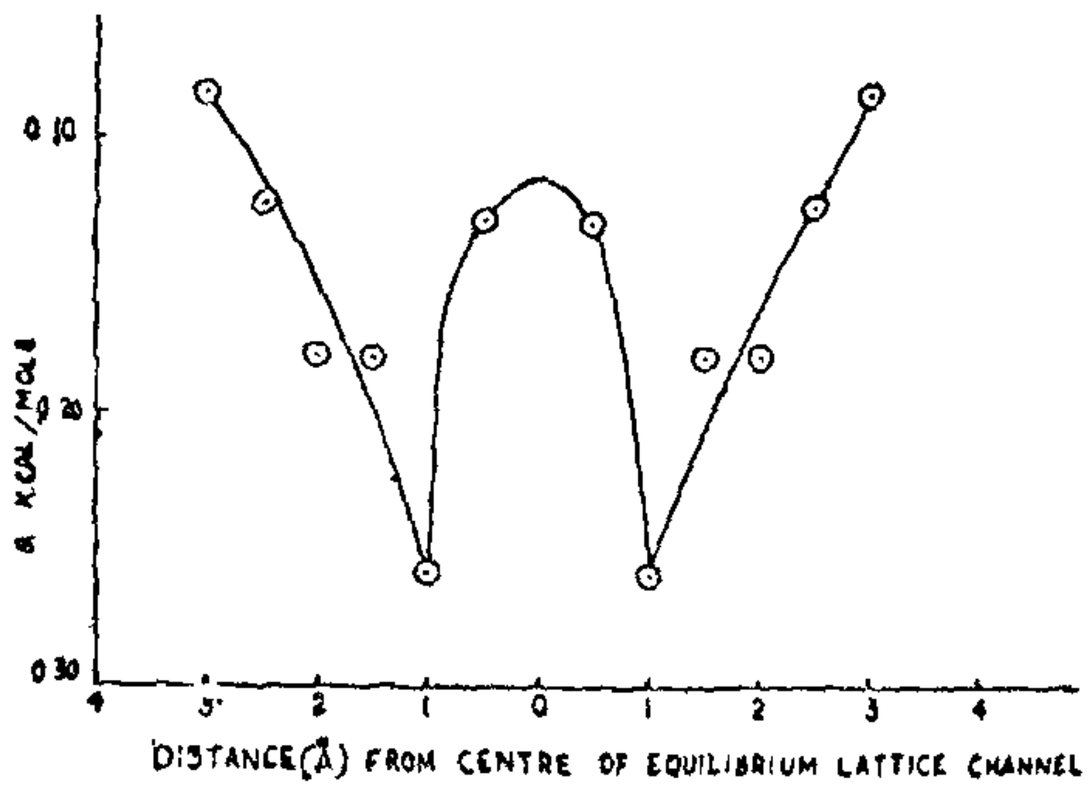

FIG. 2. Potential energy for passage of $-CH_2-$ group through the equilibrium lattice channel of urea molecule.

An experimental value was calculated for the same parameter from the urea adduct experiments. The values were calculated as follows :

The separation of *n*-paraffins by intereaction with urea at 60° C followed by cooling to room temperature was found to obey first-order kinetics (Table II). The energy of activation calculated for *n*-dodecane was 8·03 kcal/mole. Hence the value per $-CH_2-$ works out to 0·67 kcal/mole.

The near agreement for the energy of activation by theory and experiment shows that the mechanism underlying urea adduct formation with *n*-paraffins is one of penetration of urea lattice by the molecules in question.

TABLE II

Urea adduct formation with wax and dodecane

Temp. °C	Weight of urea in 80 cc of CH_3OH g	Weight of paraffin or dodecane in CCl_4 g	Weight of *n*-paraffin recovered after adduct formation g	First order rate constant $\times 10^{-4}$ sec^{-1}	Energy of activation ($\triangle E$) k.cal/mole	
Wax						
60	48	16·3/100 cc	11·9	3 634	8·125	
45	36	16·3/100 cc	8·5	2·049		
n-Dodecane						
60	48	3·4/14 cc	1·7	1·926	8·032	
45	48	3·4/14 cc	1·1	1·087		

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PREMUNITY IN WILT DISEASE OF COTTON*

V. MURUGANANDHAM AND R. KALYANASUNDARAM

University Botany Laboratory, University of Madras, Madras 600 005 (*India*)

ABSTRACT

Pre-inoculation of cotton plants (*G. arboreum* var. *indicum* L.) with a low level of a virulent strain of the pathogen *Fusarium vasinfectum* Atk. protects these plants against a subsequent inoculation of a high level of the same virulent strain.

INTRODUCTION

DURING an attempt to verify the phenomenon of cross-protection in *Fusarium* wilt of the Indian cotton, *i.e.*, *Gossypium arboreum* var. *indicum* L. (cultivar Karunganni 7) using an avirulent American strain and a virulent Indian strain of the pathogen, an unusual phenomenon was noticed. No protection was observed in the experimental plants, which were pre-inoculated *with the avirulent strain followed by a challenge inoculation* of the virulent strain. On the contrary, in one of the treatments where the virulent strain itself was used for pre-inoculation, the plants were protected against a subsequent challenge inoculation. As this was considered a very interesting phenomenon, further work was done to confirm this and these results are presented here.

EXPERIMENTAL

An Indian strain (designated I2) virulent on *G. arboreum* var. *indicum* L. and an avirulent American strain (A1) were the pathogens used[1]. Microconidial suspensions of the fungi prepared from twelve day old cultures on potato dextrose agar (PDA) were used for soil inoculation. Plants were raised from seeds in sterilized earthenware pots (*10 cm × 5 cm*) containing sterilized soil with the desired level of conidia per gram of soil. This is referred to as pre-inoculation. For challenge inoculation, the optimum level of conidia per gram of soil was added and mixed with sterilized soil prepared in fresh batches of sterilized earthenware pots. Plants from the pre-inoculated pots were removed and transplanted carefully to these pots after the roots were thoroughly washed with sterilized water, taking care not to injure the roots (Treatment 1). Plants raised in sterilized soil without pre-inoculation and transplanted to pots containing the challenge inoculation formed the control (Treatment 2). Treatment 3 consisted of plants raised in pre-inoculated soils and transferred to sterilized soil without the challenge inoculation. Treatment 4 represented the conventional pathogenicity trial done in this laboratory[2], namely, plants raised in sterilized soil receiving the optimum level of the inoculum without any further disturbance by way of transplantation.

A series of preliminary experiments confirmed that an inoculum level of 5,000 conidia per gram of soil for pre-inoculation and transplantation after 8–10

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