

### ETCH HILLOCKS ON SELENIUM

HARRISON AND SAGAR<sup>1</sup> produced pseudo-hexagonal pits on the {0001} planes and {10 $\bar{1}$ 2} pyramid planes of melt grown selenium, using bromine dissolved in methanol, as the etchant. One to one correspondence was found on the match faces of {10 $\bar{1}$ 2} planes. {10 $\bar{1}$ 0} faces did not reveal any pit formation. Henrion and Eckart<sup>2</sup> carried out etch studies on vacuum-sublimed needles of selenium. Concentrated sulphuric acid at 150° C revealed flat etch patterns in the form of rounded rectangles. The present author has carried out etching studies on melt-grown single crystals of selenium using aqueous potassium hydroxide.

A freshly cleaved sample was kept in 60% KOH at 60° C for 20 minutes. The crystal was taken out and rinsed with distilled water, methanol and ether successively and then dried in hot air.

Electron microscopy revealed that the etch features were hillocks. In order to find whether these hillocks were at dislocation sites, the sample was cleaved and the match faces had the correspondence between the hillocks on the two faces. In order to confirm, that these hillocks were at dislocation sites, the surface of the crystal was etched and then indented. The crystal was then subjected to second etching. When observed under the microscope a characteristic gathering of hillocks around the indentation mark was found.

When the etch-studies were carried out for the (10 $\bar{1}$ 0) prism plane, the hillocks were at the dislocation sites on the prism plane. Basal plane did not give favourable results thus confirming that the hillocks were at the dislocation sites.

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### KINETICS OF Ag<sup>+</sup> CATALYSED OXIDATIVE DECARBOXYLATION OF SOME ORGANIC ACIDS BY Ce<sup>4+</sup> IN H<sub>2</sub>SO<sub>4</sub> MEDIUM

IN the oxidation of various organic acids, Willard and Young<sup>1</sup> observed that formic and acetic acids were inactive towards ceric sulphate. However, many of these acids were oxidised when ceric nitrate<sup>2</sup> or

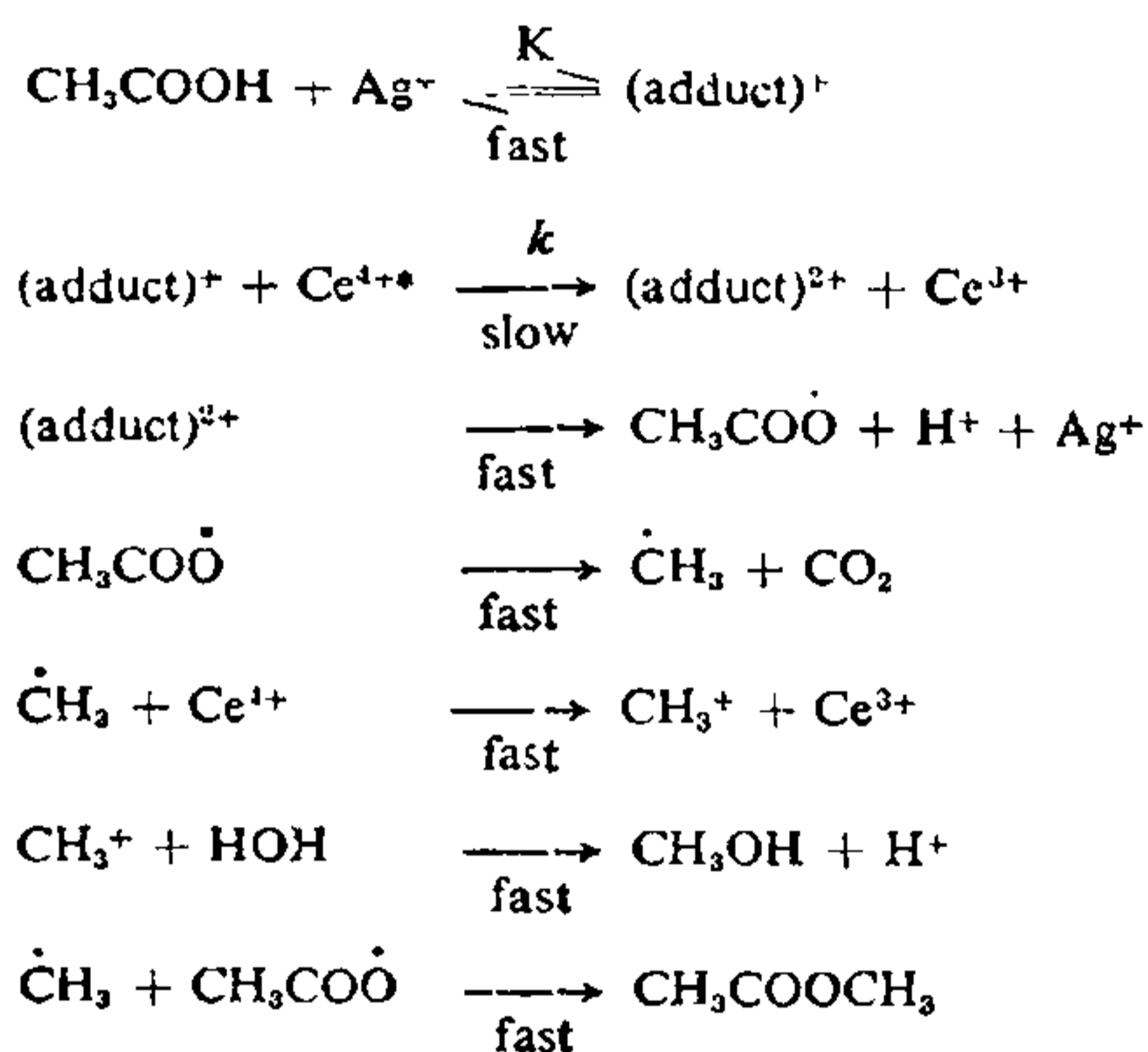
ceric perchlorate<sup>3</sup> was employed as an oxidant. Recently, it is reported that many of the aliphatic acids could be decarboxylated using a variety of oxidants<sup>4-6</sup>. In our earlier work<sup>7</sup>, it was shown that Ag<sup>+</sup> acts as a good catalyst in the oxidations involving ceric sulphate and hence, it was thought worthwhile to employ Ce<sup>4+</sup>-Ag<sup>+</sup> system in the oxidation of organic acids.

All the chemicals used were of reagent grade and the method of following the kinetics was the same as in our earlier paper<sup>8</sup>. Under conditions of [Ce<sup>4+</sup>]  $\ll$  [organic acid] in the presence of constant amount of [Ag<sup>+</sup>] the order of [Ce<sup>4+</sup>] was found to be unity. The pseudo-first order rate constants ( $k'$ ) were calculated from the slope of the plot of  $\log a/a-x$  vs. time. The order with respect to all the organic acids obtained from the  $\log k'$  vs  $\log$  [organic acid] plots was found to be fractional. Increase in [Ag<sup>+</sup>] increases the rate and the order of [Ag<sup>+</sup>] was also fractional in all the cases. [Ag<sup>+</sup>] was found to be unchanged at the end of the reaction as indicated by the constant thiocyanate titre value. Increase in [H<sup>+</sup>] from 0.1 M ( $k' = 7.9 \times 10^{-3} \text{ min}^{-1}$ ) to 0.7 M ( $k' = 21.9 \times 10^{-3} \text{ min}^{-1}$ ) at 52° C and at constant ionic strength ( $\mu = 1.9 \text{ M}$ ) shows that H<sup>+</sup> accelerates the rate. Increase in sulphate or bisulphate concentration decreases the rate. The reactions were studied in the temperature range 45-65° to evaluate the activation energy.

Ag<sup>+</sup> catalysis of Ce<sup>4+</sup> oxidations was first observed by Sinha<sup>9</sup> in the Ce<sup>4+</sup> - Tl<sup>+</sup> reaction. The order of unity observed for [Ag<sup>+</sup>], [Ce (NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> and [Tl<sup>+</sup>] was explained with the aid of Ag<sup>2+</sup> assumed to have been formed from the reaction between Ag<sup>+</sup> and a complex species TlH[Ce (NO<sub>3</sub>)<sub>6</sub>]. Higginson *et al.*<sup>10</sup> also postulated an intermediate Ag<sup>2+</sup> in the Tl<sup>+</sup> and Hg<sub>2</sub><sup>2+</sup> oxidations by Ce<sup>4+</sup>. Both these groups of workers assumed that the oxidation of Tl<sup>+</sup> takes place by Ag<sup>2+</sup> in a subsequent step. One significant observation of the latter workers is that in the absence of a suitable substrate no reaction was possible between Ce<sup>4+</sup> and Ag<sup>+</sup>. The fractional order of organic acid indicates that it may be involved in the complex formation either with Ce<sup>4+</sup> or Ag<sup>+</sup>. Spectral studies in the present work indicated no complexation between Ce<sup>4+</sup> and organic acid in conformity with our earlier observations<sup>8</sup>. This, as well as the effect of [H<sup>+</sup>], [sulphate], and [bisulphate], which shows a similar trend reported earlier for other substrates, indicates that neutral Ce (SO<sub>4</sub>)<sub>2</sub> is the reactive species. Ag<sup>+</sup> is known to form colourless adducts with oxygen containing compounds with a lone pair of electrons on oxygen atom<sup>11</sup>. It is therefore not unreasonable to assume

the formation of an adduct between  $\text{Ag}^+$  and organic acid before oxidation by  $\text{Ce}^{4+}$  occurs in a slow step to yield  $\text{Ag}^{2+}$ -substrate adduct. The formation of  $\text{Ag}^{2+}$ -substrate adduct was confirmed by adding bipyridyl to the reaction system which gave brown coloured bipyridyl complex of  $\text{Ag}^{2+}$  with its characteristic absorption maximum at 454 nm<sup>12</sup>.

If the adduct formation is taken as the first step, the reaction scheme for the  $\text{Ce}^{4+} - \text{CH}_3\text{COOH}$  reaction (taken as a typical example) in the presence of  $\text{Ag}^+$  could be written as follows:



\*  $\text{Ce}(\text{SO}_4)_2$  is written as  $\text{Ce}^{4+}$  for simplicity.

From the above mechanism the rate equation comes out to be

$$-\frac{2.303 d \log [\text{Ce}^{4+}]}{dt} = k' = \frac{Kk [\text{Ag}^+] [\text{CH}_3\text{COOH}]}{1 + K [\text{CH}_3\text{COOH}] + K [\text{Ag}^+]} \quad (1)$$

where  $k'$  is the observed pseudo first order rate constant obtained from the plot of  $\log a/a - x$  vs time,  $k$  is the bimolecular rate constant for the slow step and  $K$  the formation constant of the adduct. Equation (1) accounts for the first order dependence of rate on  $[\text{Ce}^{4+}]$  and fractional order dependence on  $[\text{Ag}^+]$  and [organic acid] obtained experimentally.

Taking the reciprocal of the equation (1) we get

$$\frac{1}{k'} = \frac{1}{[\text{CH}_3\text{COOH}]} \left[ \frac{1}{Kk [\text{Ag}^+]} + \frac{1}{k} \right] + \frac{1}{k [\text{Ag}^+]} \quad (2)$$

From equation (2) it is clear that the plots of  $1/k'$  vs  $1/[\text{organic acid}]$  at constant  $[\text{Ag}^+]$  should be linear. Such plots were obtained in the present work for all the acids studied. From the intercept and slope the bimolecular rate constant for the slow

step ( $k$ ) and formation constant for the adduct ( $K$ ) were evaluated (Table I).

TABLE I

Name of the acid	$k \times 10^3$ $\text{l mol}^{-1} \text{sec}^{-1}$	$K \text{ l mol}^{-1}$	$\Delta E^\ddagger$ Kcals $\text{mol}^{-1}$
Acetic acid	5.6	1.09	22.9
Propionic acid	21.0	1.20	22.0
Iso-butyric acid	29.7	9.27	18.3
Pivalic acid	45.0	33.89	13.1
<i>n</i> -Butyric acid	22.2	2.24	17.7
<i>n</i> -Valeric acid	23.1	3.50	17.2
Iso-valeric acid	23.0	4.50	13.7

Due to inductive effect of the methyl groups, its substitution in  $\text{CH}_3\text{COOH}$  reduces the strength of the corresponding acids. The inductive effect of the alkyl groups increases in the order:  $\text{CH}_3 < \text{CH}_3\text{CH}_2 < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}$ <sup>13</sup>. The increase in electron density on hydroxyl oxygen favours the formation of  $\text{Ag}^+$ -carboxylic acid adduct. This is clearly indicated from the formation constants calculated from kinetic studies in the present work (Table I). For the same reason the bimolecular rate constants ( $k$ ) for the slow step should also show a similar trend. That this is so, is clear from Table I. The acidity constants data<sup>13</sup> indicate that *n*-butyric, *n*-valeric and iso-valeric acids are weaker than acetic acid and hence, should have higher  $K$  value. The  $K$  and  $k$  values follow this trend (Table I) and confirm indirectly the formation of  $\text{Ag}^+$ -acid adducts.

The plot of  $\Delta H^\ddagger$  vs  $\Delta S^\ddagger$  is linear with a slope equal to 350 which is the isokinetic temperature. The isokinetic temperature is greater than the temperature range used in the present study (318–338° K) indicating that the reactions are enthalpy controlled, as is evident from Table I.

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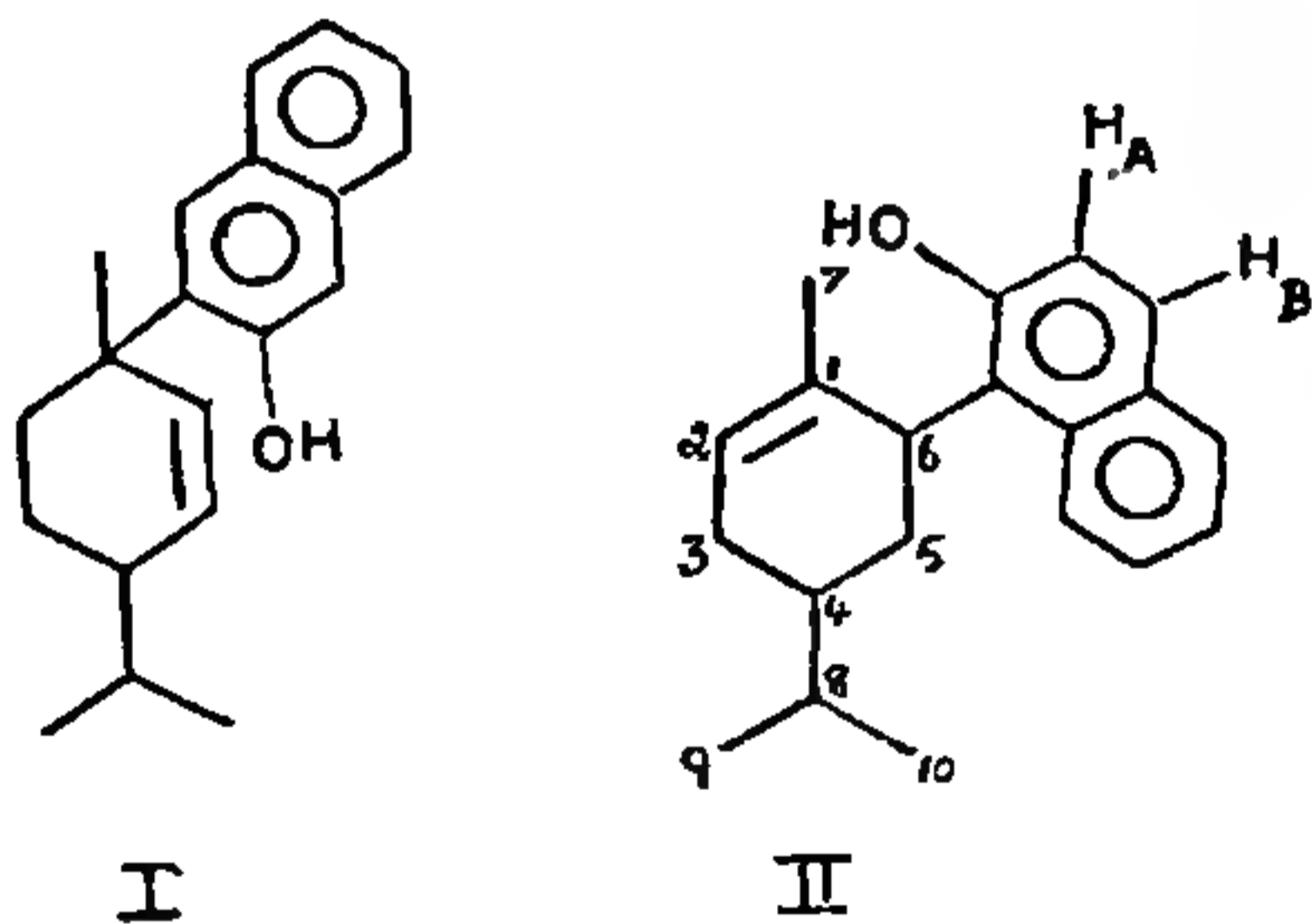
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### REVISED STRUCTURE FOR THE ADDUCT OF $\alpha$ -PHELLANDRENE WITH $\beta$ -NAPHTHOL

INCORPORATION of  $\beta$ -naphthol to  $\alpha$ -phellandrene gave an adduct  $C_{20}H_{24}O$ , m. p. 139-140° for which Salfeld<sup>1, 2</sup> assigned structure (I). We now propose structure (II) for this derivative based on its spec-



tral properties: ir (nujol): 3400 (-OH), 1630

( $\text{>C=C<}$ ): 1380, 1375, 1165 ( $-\text{CH}<\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ );

$850\text{ cm}^{-1}$  ( $\begin{matrix} \text{R}_1 \\ \text{R}_2 \end{matrix} \text{C}=\text{C} \begin{matrix} \text{R}_3 \\ \text{H} \end{matrix}$ ); nmr ( $\text{CCl}_4$ ) (60 MHz);

$\delta$  7.7 (multiplet, 4 H; aromatic protons); 7.60, 7.47, 7.07, 6.94 (AB quartet, J 8 Hz; 2 H; aromatic protons  $\text{H}_A$  and  $\text{H}_B$ ); 6.1 (singlet, 1 H; -OH); 5.5 (broad singlet  $\text{W}_2$ , 8 Hz; 1 H;  $\text{C}_2\text{H}$ ); 4.1 (broadened doublet,  $\text{J}_{6,5a,7}$  11 Hz,  $\text{J}_{6,5c,7}$  small; 1 H;  $\text{C}_6\text{H}$ ); 1.7 (doublet, J 1 Hz; 3 H;

$\text{C}_7-\text{CH}_3$ ); 0.8 [obscured pair of doublets; J 7 Hz; 6 H; ( $-\text{CH}<\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ )]

Further details will be published elsewhere.

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### OCCURRENCE OF *KECKIA ANNULATA* GLOCKER, IN THE BAGH BEDS OF NARMADA VALLEY

OCCURRENCE of *Keckia annulata* Glocker a Cenomanian Trace Fossil from Germany, in the Nimar Sandstone (Fig. 1) is of interest because of the information it yields about the ethological conditions during the deposition of the Bagh Beds.

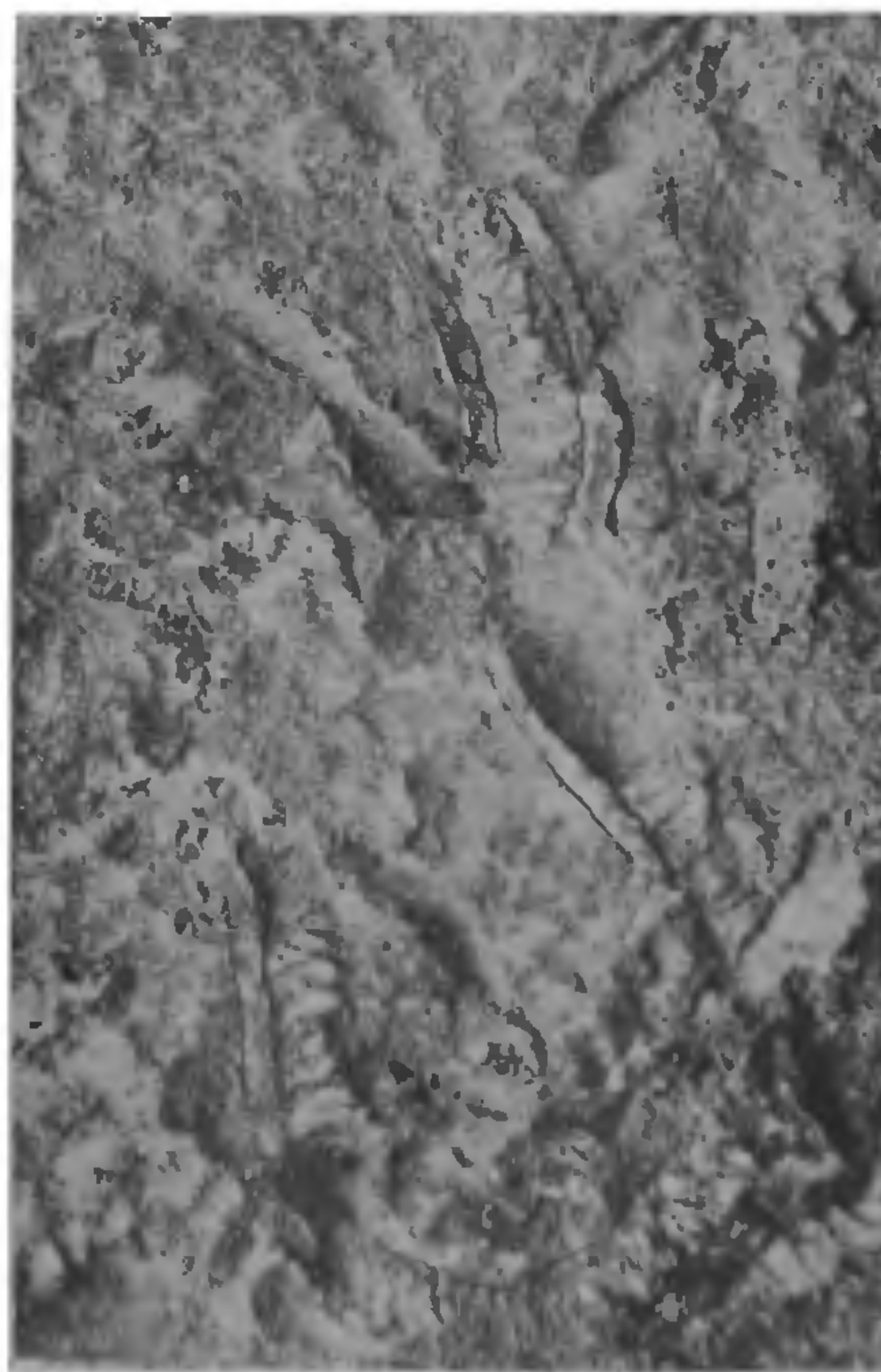


FIG. 1. *Keckia annulata* Glocker, showing feeding burrows along bedding plane and holes approaching the bedding plane,  $\times 1$ .