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BROMINATION OF BENZENE AND SUBSTITUTED BENZENES WITH POTASSIUM BROMATE.—A KINETIC STUDY

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ALTHOUGH potassium bromate in sulphuric acid is to known[1] to brominate benzene into bromobenzene, potassium bromate has hardly ever been used as a brominating agent for aromatics. It is only in the last two years that some interest has been shown on the synthetic utility in reactions[1,2]. Yet, no kinetic work is on record to determine the mechanism of this reaction. We report in this communication, the preliminary results of such an investigation.

Benzene and other aromatics (both deactivated as well as activated) undergo facile bromination in aqueous acetic acid in the presence of added sulphuric acid. These are conditions under which very little reaction takes place with molecular bromine. The amount of sulphuric acid needed obviously varies with the system—deactivated aromatics requiring a much larger percentage of the mineral acid. The reactions follow a simple rate-law. For the bromination of benzene.

$$\frac{-d\,[\mathrm{Br}(V)]}{dt} = k_2\,(\text{benzene})\quad [\mathrm{Br}(V)]$$

No simple correlation could be established between rate and acidity. Due to the electrophilic nature of the reagent, the highest rates are obtained with activated aromatics such as toluene or *p*-xylene. Tables 1 and 2 summarize some of the data for these experiments. The rates were followed by an iodometric assay of the unracted bromate (V) at suitable time intervals under pseudo first-order conditions.

TABLE 2

Substrate	$10^5 k_1 \mathrm{sec}^{-1}$
Benzene*	4.64
Toluene*	39.17
p-cxylene*	90.3
Acetanilide*	333
Benzoic acid§	34.4
Nitrobenzene§	2.69
Chlorobenzene§	256
Benzene§	938
[Substrate]=0.05M	Temp: 50° C
$[BrO^-_3]$=0.005M	Solvent: 50% HOAC-50% H_2O

*1.0M H_2SO_4
§3.0M H_2SO_4.

As the deactivated aromatics lead to a single product (*viz.* the meta-nitroderivative), the data for benzoic acid and nitrobenzene in table 2 (with that for benezene, statistically corrected for the six nuclear positions) was subjected to a Hammett analysis using the Brown-Okamoto σ values. The Hammett rho of −3.1, though on the low side, underscores the electrophilic nature of the substitution process.

TABLE

[Benzene] M	$[BrO^-_3]$ M	$10^5.k_1 \mathrm{sec}^{-1}$ $[H_2SO_4]$	$10^4 k_2$ lit.mol.$^{-1}$ sec^{-1}	
0.05	0.004	1	4.62	9.20
0.05	0.005	1	4.64	9.28
0.05	0.007	1	4.58	9.16
0.07	0.005	1	6.58	9.40
0.10	0.005	1	9.56	9.56
0.05	0.005	2	343	
0.05	0.005	3	938	
Temp: 50° C		Solvent: 50% HOAc 50% H_2O		

It is premature to comment on the actual brominating agent in this reaction with the present data—it is certainly not free molecular bromine; Harrison (*loc.cit*) is of the opinion that Br_2 even if formed would be converted into H_2O Br in strong sulphuric acid which would be the brominating agent.

$$Br_2 + H_3O^{\oplus} \rightarrow H_2O^{+}Br + HBr$$

Further work on the elucidation of the mechanism of this reaction is in progress.

8 October 1982

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THE FIRST RECORD OF EARLY STONE AGE TOOLS OF MAN FROM GHUMARWIN, HIMACHAL PRADESH

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HARITALYANGAR area of Ghumarwin in the district Bilasput (Himachala Pradesh) is well known for fossils of the earliest hominoid ancestors of man but stone tools of palaeolithic man are not reported so far from this and other adjoining areas. The present author discovered the first evidence of stone tool[1] (see Figure 1) during July 1979 but subsequently recovered some more tools (Figure 2, 3, 6 & 13 to 15) during a search for hominoid fossils in the years 1980 and 1981. It was however, only very recently (February 1982) that the author recovered a large number of stone tools and artefacts some of which are illustrated in the figure (Figure 4, 5 & 7 to 12). The present communication is the first report of these findings from Ghumarwin area and is significant as it provides an intermediate bridge between the two well known prehistoric sites of Himachal Pradesh, *viz* the Beas–Banganga valley in Kangra[2-4] and the Sirsa Valley in Nalagarh[5].

The stone tools were recovered near Baron, west of Bhapral (No. 1), Kasohal (No. 2), Tarauntra (nos. 3 & 6) and the rest near Lehri Sarail. The latter locality has yielded a large number of artefacts and discarded chipped pebbles. The tools were recovered from slopes of the Sivaliks in the vicinity of the *choes* which meet *Sir Khad*- a tributary of the Sutlej. Typologically

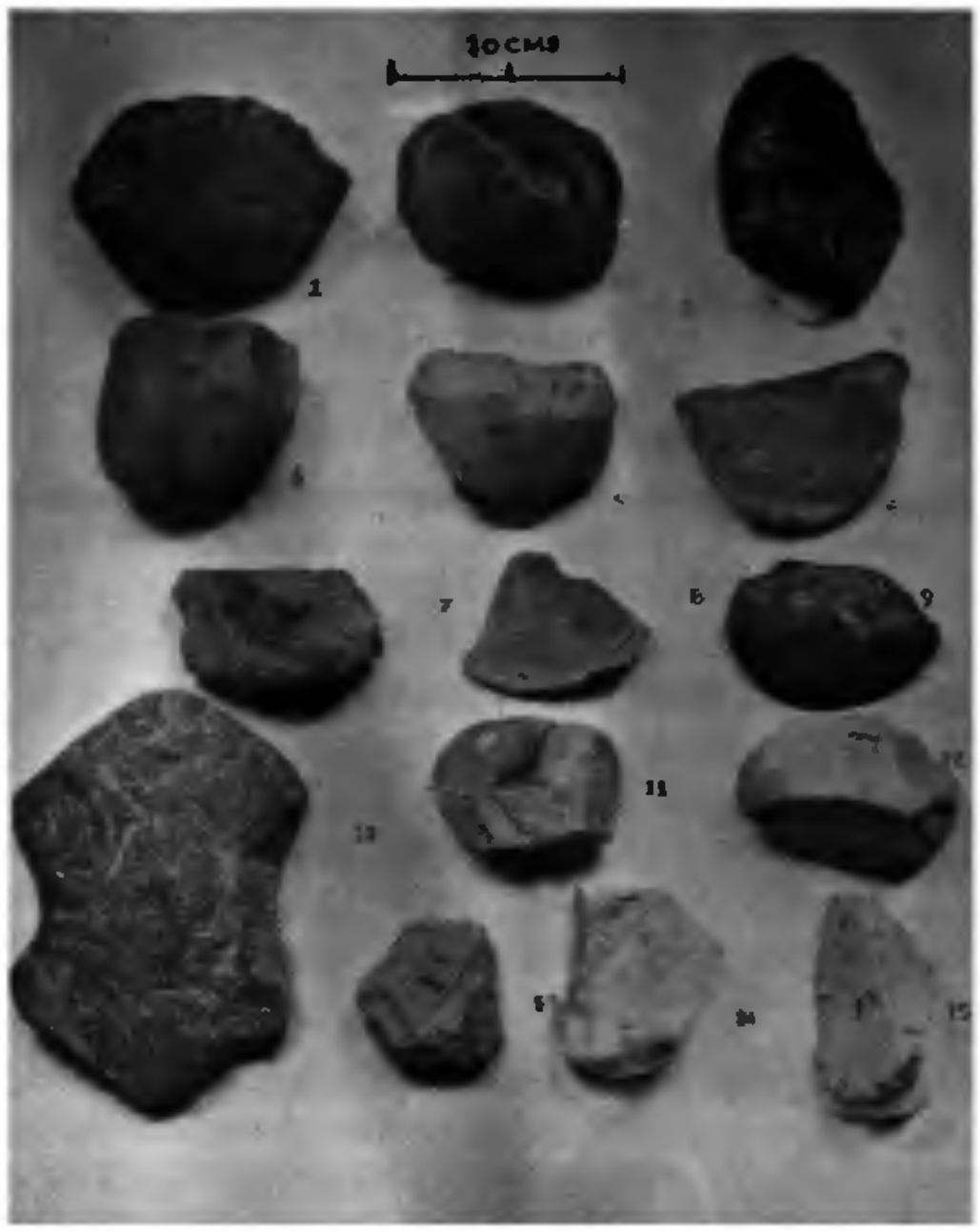

Figure 1 to 15 Early Stone Age Tools from Ghumarwi.

the implements sampled as chopper–chopping tool or bifacial chopper (No. 1), choppers (Nos. 2 to 4), cleaver (No. 10), and several cores and flakes which could serve as scraping devices. Except a few chert cores and flakes (Nos. 13 to 15) recovered from Lehri Sarail, all tools are made with quartzite pebbles. Multiple scars of free primary flaking are noticeable on the tools with minor retouching in some cases.

Typo-technologically the present findings are comparable with the Beas–Banganga tools and equatable to the Early Soanian pebble tradition of Potwar region. The present evidence reveals a continuously southwardly movement of Soan Man through the sub-Himalayan terrain. Detailed studies of the tool collection and more systematic investigation of the area are contemplated for further details.

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