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KINETIC EVIDENCE FOR HYDROBROMIC ACID CATALYSIS IN n- BUTYL BROMIDE PHOTOBROMINATION.

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From the kinetic study of n-butyl bromide photobromination, we show, in the present communication, that two reaction mechanisms are operative. In the early stages, an uncatalysed process is observed; when enough hydrobromic acid is produced, a second catalysed reaction becomes significant.

The change in mechanism almost certainly parallels the selectivity modifications observed by TANNER ([1]). Normal selectivity is afforded by the uncatalysed mechanism while autocatalysis preferentially leads to 1-2 dibromides. So far, anchimeric assistance has been considered to be the only substantial explanation of the observed selectivity in bromides radical brominations ([2-9]). Here, a bridged radical associated with hydrobromic acid catalysis appears to be the conditions of enhanced selectivity.

Since very small amounts of hydrobromic acid seem to be sufficient to improve the yields of 1-2 dibromo-isomers ([1]), the kinetics of 1-bromobutane photobromination have been investigated. When bromine disappearance is followed, at different initial concentrations, autocatalysis is observed.

In other experiments, carbon tetrachloride, saturated with hydrogen bromide, was added to the reaction mixtures prior to starting irradiation. The half-life period of bromine was shortened (from 16.5 min. without CCl_4 - HBr, to 2.5 min. with 7% in volume of CCl_4 - HBr).

In the next experiments, 1-bromobutane was saturated with gazeous hydrobromic acid. Photobromination of such solutions (large excess of butyl bromide and hydrobromic acid at constant concentration) allowed us to determine partial order of the reaction versus bromine. After four different runs, a mean value of 1.5 was found, leading to the integrated rate expression (1):

$$1/\sqrt{[Br_2]_t} = 1/\sqrt{[Br_2]_o} + k''_{1.5}t/2 \qquad (1).$$

A last set of experiments was performed with neat n-butyl bromide as starting material. The partial order versus hydrogen bromide is shown to be two, except in the early stages of the reaction, where order zero is found - see figure.

In conclusion, our present results led us to consider the whole rate equation:

$$V/[Br_2]^{3/2} = k'_o + k'_c [HBr]^2 \qquad (2).$$

$$V = \{k'_o + k'_c [HBr]^2\} \cdot [Br_2]^{3/2} \qquad (3).$$

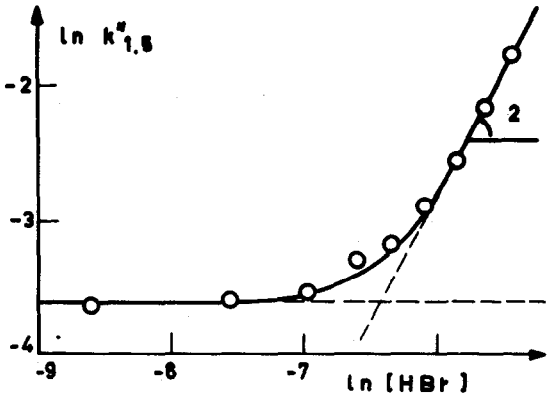

Figure: Determination of the partial order versus hydrogen bromide.

$[HBr]_t = [Br_2]_o - [Br_2]_t$.

The results obtained were in agreement with the preceeding relation - see Table.

Experiment.	$10^6\ k'_c$ (a)	k'_o (a)	r (b)
1	0.113 ± 0.003	0.29 ± 0.02	0.998
2	0.082 ± 0.001	0.23 ± 0.02	0.999
3	0.175 ± 0.004	1.31 ± 0.06	0.994
4	0.238 ± 0.006	0.97 ± 0.04	0.995
5	0.134 ± 0.003	0.71 ± 0.09	0.993
6	0.163 ± 0.003	1.30 ± 0.06	0.997

$\begin{cases} k'_o \text{ in } M^{-\frac{1}{2}}\ L^{\frac{1}{2}}\ min.^{-1}. \\ k'_c \text{ in } M^{-5/2}\ L^{5/2}\ min.^{-1}. \end{cases}$

Table: Values of parameters obtained from least square method applied to equation (2).

(a): Variations between values of kinetic constants can be attributed to slightly different optical conditions between various runs.

(b): Correlation coefficient.

According to this, bromine should disappear by two pathways: k'_o and k'_c are the rate constants for the uncatalysed and catalysed processes, respectively.

Experiments to find a plausible mechanistic explanation of the kinetic data are now in progress.

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