KINETICS AND MECHANISM OF OXIDATION OF ACETONE BY N-BROMOACETAMIDE IN ACIDIC MEDIA

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ABSTRACT

Kinetics of oxidation of acetone by N-bromoacetamide (NBA) in perchloric acid medium in the presence of mercuric acetate has been reported in the temperature range 30–50°C. A zero order dependence to NBA and a first order dependence to both acetone and hydrogen ion concentration have been observed. Insignificant effect of acetamide, mercuric acetate and sodium perchlorate has been observed on the reaction rate. A negative dielectric effect and a solvent isotope effect have been observed. Various rate parameters have been computed and formic and acetic acids were identified as the end products. A suitable mechanistic route for the oxidation by NBA in acidic media has been suggested.

INTRODUCTION

N-BROMOACETAMIDE (NBA) has earlier been used as an oxidising and halogenating reagent[1] in preparative organic chemistry. Kinetic investigations involving alcohols[2], dimethyl sulphoxide[3] and some ketones[4] as substrates and NBA as oxidant have been recently reported. Relatively little work has however been carried out on the oxidative kinetics involving NBA and the mechanistic interpretation of the results is obscure. The present communication incorporates the results of the kinetics of oxidation of acetone by NBA in acidic media. The main aim has been to explore the mechanistic route for this particular redox process.

EXPERIMENTAL

The chemicals employed were of A.R. quality. NBA solution was prepared fresh and its strength was checked iodometrically. Deuterium oxide (99.4%) was supplied by BARC, Bombay (India). Triple distilled water was used throughout the investigation and the reaction stills were opaque to light to avoid any photochemical effect.

The reaction was initiated by adding the approximate volume of acetone to a mixture containing suitable amounts of NBA, perchloric acid, mercuric acetate and all other reagents, maintained at a constant temperature ($\pm 0.1°C$). The kinetics was followed by estimating unconsumed NBA iodometrically at regular intervals of time (error = $\pm 2.08\%$).

Results: The stoichiometry of the reaction was determined with varying amounts of NBA in excess of acetone. The estimation of unconsumed NBA in all sets showed that 1 mol of acetone consumed 3 mol of NBA. Accordingly, the following stoichiometric equation can be formulated:

$$3MeCONHBr + CH_3COCH_3 + 3H_2O$$
$$\rightarrow 3MeCONH_2 + HCOOH$$
$$+ CH_3COOH + 3HBr \qquad (1)$$
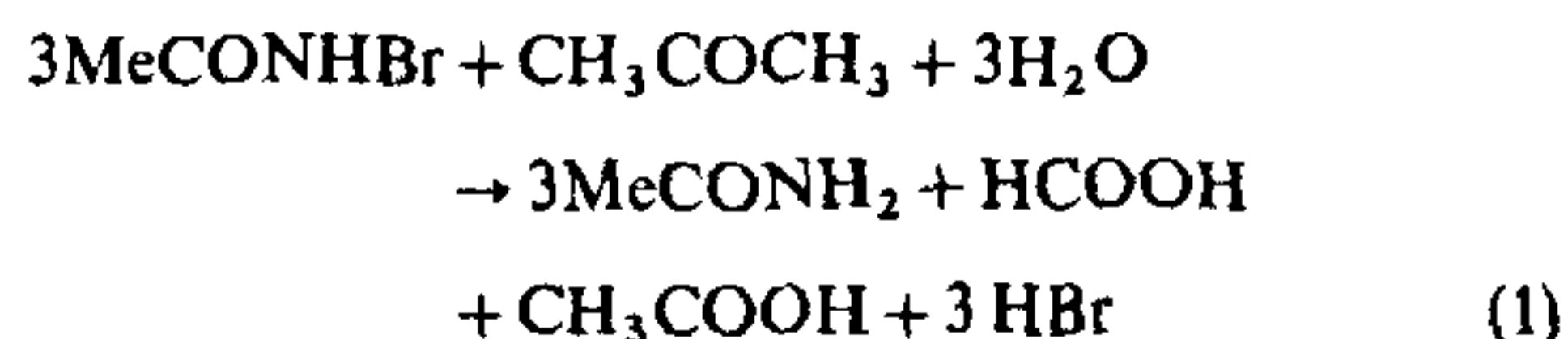
Formic and acetic acids as end products were identified by adopting TLC followed by conventional spot test analysis[5].

Variation of concentration of the reactants showed that the reaction followed zero order kinetics in NBA which was further supported through the plots of the remaining [NBA] and time for varying concentrations of NBA. A set of parallel lines confirmed zero order dependence on NBA. An increase in acetone concentration increased the zero order rate constant linearly, indicating first-order in acetone, which was further confirmed by log k_0 vs log [acetone] plot yielding slope value nearly one (0.98, 1.02, 1.04 and 0.96. The average values of first order rate constants k'_1 ($k'_1 = k_0/[\text{acetone}]$) were 1.27 and 1.92 × 10^{-3} min^{-1} at 35° and 40°C, respectively. Table 1 records the results at varying [H$^+$], [acetamide], [Hg(OAc)$_2$] and at different ionic strength (μ) of the medium. Constancy in k'_1 ($k'_1 = k_0/[\text{HClO}_4]$) values showed first order in hydrogen ions. The average values of first order rate constants were (1.57 and 2.37) × 10^{-4} min^{-1} at 35° and 40°C, respectively. Acetamide, mercuric acetate and sodium perchlorate (added for ionic strength variation) additions had zero effect on reaction rate.

Table 1 Effect of $[H^+]$, $[acetamide]$, $[Hg\,(OAc)_2]$ and ionic strength (μ) variation on rate.

$[NBA] = 0.97 \times 10^{-3}$ M, $[acetone] = 2.00 \times 10^{-2}$ M
$[Hg(OAc)_2] = 1.20 \times 10^{-3}$ M (unless otherwise stated).

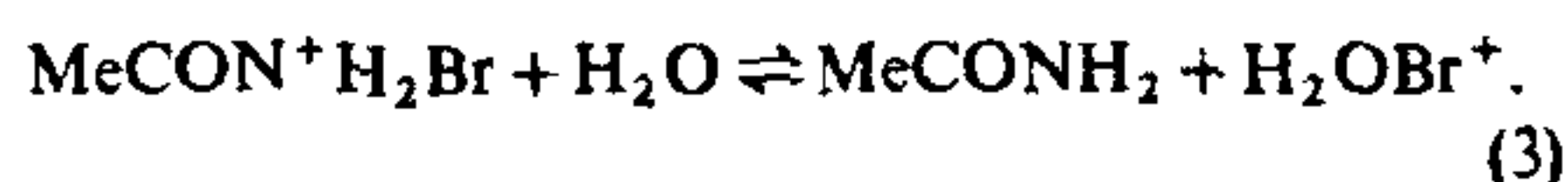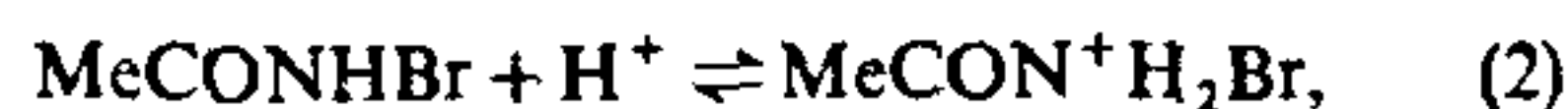| $[HClO_4]\,10^2$	$10^5 k_0$ mol l^{-1} min^{-1}		$[HClO_4]\,10^2$	$10^5 k_0$ mol l^{-1} min^{-1}	
M	35°	40°	M	35°	40°
3.30	0.54	0.82	12.40^c	1.90	3.00
5.00	0.78	1.19	12.40^d	1.92	3.02
6.40	0.97	1.50	8.00^e	3.14	4.72
8.00	1.30	1.90	8.00^f	3.15	4.70
12.40	1.91	2.90	8.00^g	3.13	4.76
16.00	2.47	3.72	8.00^h	3.14	4.72
20.00	3.10	4.70	5.00^i	0.78	1.15
12.40^a	1.91	3.05	5.00^j	0.76	1.20
12.40^b	1.92	3.02	5.00^k	0.78	1.17

[Acetamide] $= 2$(a), 4(b), 6(c) and 8×10^{-3} M(d)
$\mu = 8.36$(e), 8.80(f), 12(g) and 16×10^{-2} M(h) at [acetone] $\approx 5 \times 10^{-2}$ M.
$[Hg(OAc)_2] = 1.6$(i), 2(j) and 3×10^{-3} M (k).

Successive additions of acetic acid to the reaction mixture showed positive effect on the reaction rate, indicating involvement of at least a dipolar molecule in rate controlling step. The results of experiments on 40%, 60% and 80% D_2O (V/V) are given in table 2, which also includes the data obtained at 30°, 35°, 40°, 45° and 50°C. The rate measurements at these temperatures led to compute activation energy, $\Delta E^{\neq}$ (18.30 K cal/mol), frequency factor, A(1.24 $\times 10^9$ l mol^{-1} sec^{-1}), heat of activation, $\Delta H^{\neq}$ (17.69 K cal/mol), entropy of activation, $\Delta S^{\neq}$ (-17.87 e.u.) and free energy of activation, $\Delta E^{\neq}$ (23.20 K cal/mol).

DISCUSSION

NBA is known to exist in acidic media in the following equilibria:

$$MeCONHBr + H^+ \rightleftharpoons MeCON^+H_2Br, \quad (2)$$

$$MeCON^+H_2Br + H_2O \rightleftharpoons MeCONH_2 + H_2OBr^+. \quad (3)$$

There may thus be three possible oxidising species, namely, NBA itself, H_2OBr^+, or protonated NBA, that is, $MeCON^+H_2Br$ (N^+BAH) which can participate in the reaction.

Br_2 is scavenged by mercuric acetate[6] as unionized

Table 2 Effect of D_2O and acetic acid additions and temperature variations on reaction rate

$[NBA] = 0.97 \times 10^{-3}$ M, $[acetone] = 2 \times 10^{-2}$ M
$[HClO_4] = 5 \times 10^{-2}$ M and $[Hg(OAc)_2] = 1.2 \times 10^{-3}$ M

| Temp. °C	D_2O-H_2O V/V (%)	Acetic acid-H_2O V/V(%)	$10^6 k_0$ mol l^{-1} min^{-1}	
35	0-100	0-100	7.80	13.40*
35	40-60	0-100	14.04	24.12*
35	60-40	0-100	15.12	26.00*
35	80-20	0-100	16.00	27.47*
35	0-100	25-75	9.20	17.00*
35	0-100	40-60	13.36	21.24*
35	0-100	60-40	15.96	25.98*
30	0-100	0-100	5.00	—
35	0-100	0-100	7.80	—
40	0-100	0-100	13.40	—
45	0-100	0-100	21.20	—
50	0-100	0-100	32.30	—

* Temp. at 40°C.

HgBr$_2$ and thus the possibility of any possible bromine oxidation is completely masked, which would have formed as a result of an interaction between NBA and HBr as follows:

$$MeCONHBr + HBr \rightarrow MeCONH_2 + Br_2. \quad (4)$$

Thus the addition of mercuric acetate ensures the oxidation through pure NBA.

Ketones form oxonium salts on protonation in the presence of strong acids. Since oxygen is more electronegative than carbon, the second resonating structure makes a larger contribution than the first

$$\rangle C=O+H^+ \rightleftharpoons \rangle \underset{(I)}{C=O^+H} \leftrightarrow \rangle C^+ \underset{(II)}{-O-H} \quad (5)$$
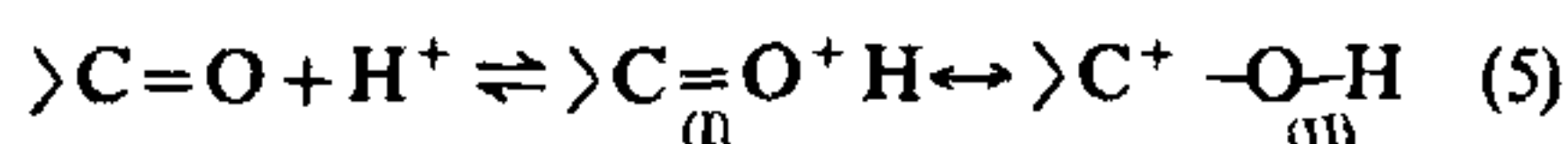
If H$_2$OBr$^+$ is taken as the real oxidising species of NBA, the mechanism thus proposed would give a rate law (6) which requires inverse proportionality of the reaction rate with acetamide
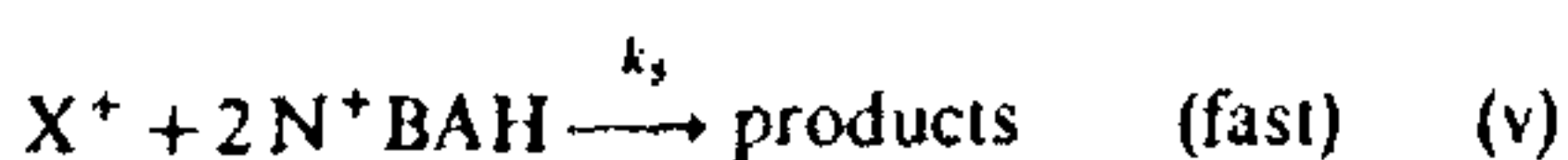
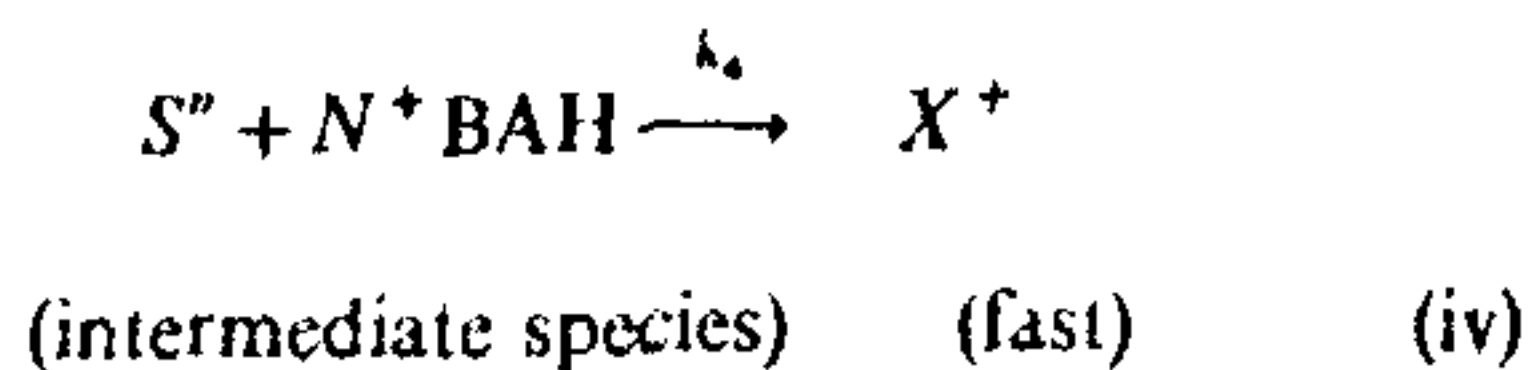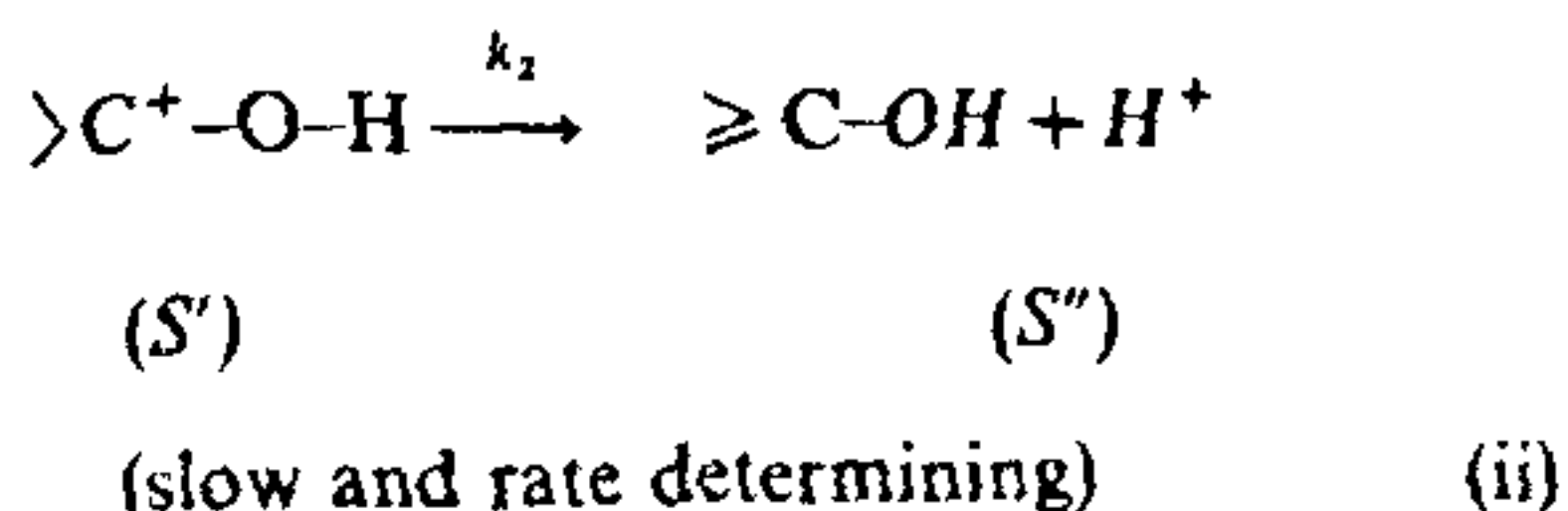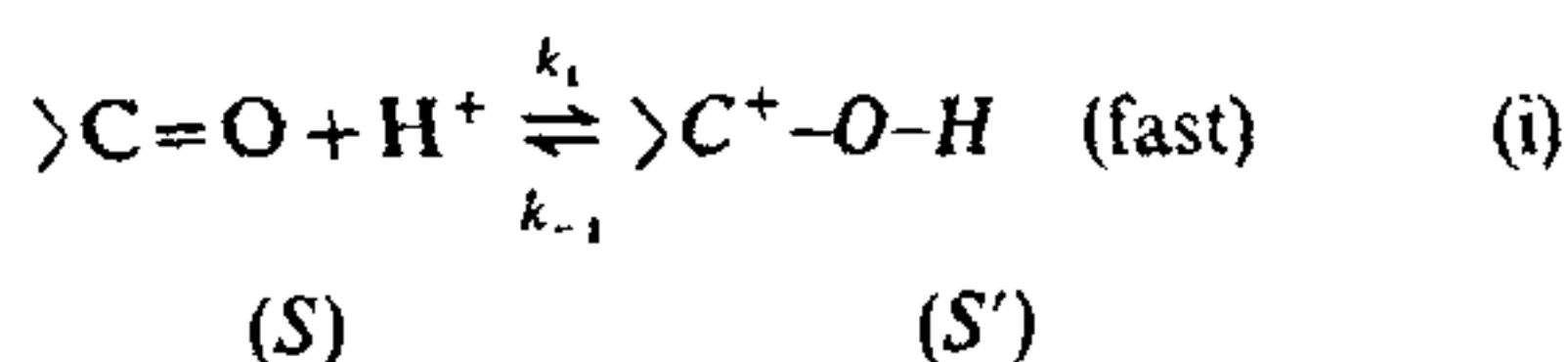$$-\frac{d[NBA]}{dt} = k\frac{[Acetone][H^+]}{[M]} \quad (6)$$

(where $k = 3k_2k_4k''/k_{-3}$ and $M = $ Acetamide)

concentration contrary to our observed zero acetamide effect. Hence H$_2$OBr$^+$ as possible oxidising species is ruled out.

Considering zero order in NBA and contention of Littler and Waters[7] that in such cases enolisation step will be slow and rate determining, the following two mechanistic schemes are suggested in which S represents acetone, S' the conjugate acid and S'' the enol form.
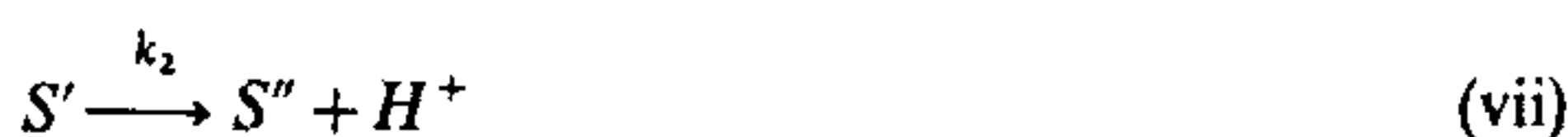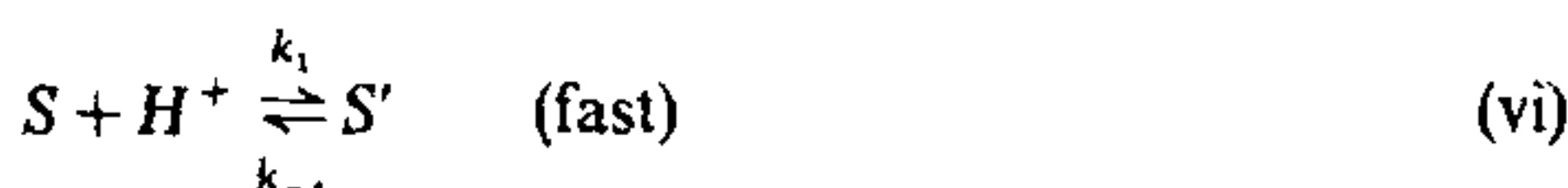
Scheme 1

N$^+$BA as oxidising agent.

$$\rangle C=O+H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \rangle C^+ -O-H \quad (fast) \quad (i)$$
$$(S) \qquad\qquad (S')$$

$$\rangle C^+ -O-H \overset{k_2}{\longrightarrow} \geqslant C-OH + H^+$$
$$(S') \qquad\qquad (S'')$$

(slow and rate determining)   (ii)

$$NBA + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} N^+BAH \quad (fast) \quad (iii)$$

$$S'' + N^+BAH \overset{k_4}{\longrightarrow} X^+$$

(intermediate species)   (fast)   (iv)

$$X^+ + 2N^+BAH \overset{k_5}{\longrightarrow} products \quad (fast) \quad (v)$$

Application of the steady state treatment to S' yields the rate law (7) as

$$-\frac{d[NBA]}{dt} = \frac{3k_1}{(k_{-1}+k_2)}[S][H^+] \quad (7)$$

Scheme 2

NBA as oxidising species.

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S' \quad (fast) \quad (vi)$$

$$S' \overset{k_2}{\longrightarrow} S'' + H^+ \quad (vii)$$

Slow and rate determining

$$S'' + NBA \overset{k_3}{\longrightarrow} Y$$

(intermediate species)   (fast)   (viii)

$$Y + 2NBA \overset{k_4}{\longrightarrow} products \quad (fast) \quad (ix)$$
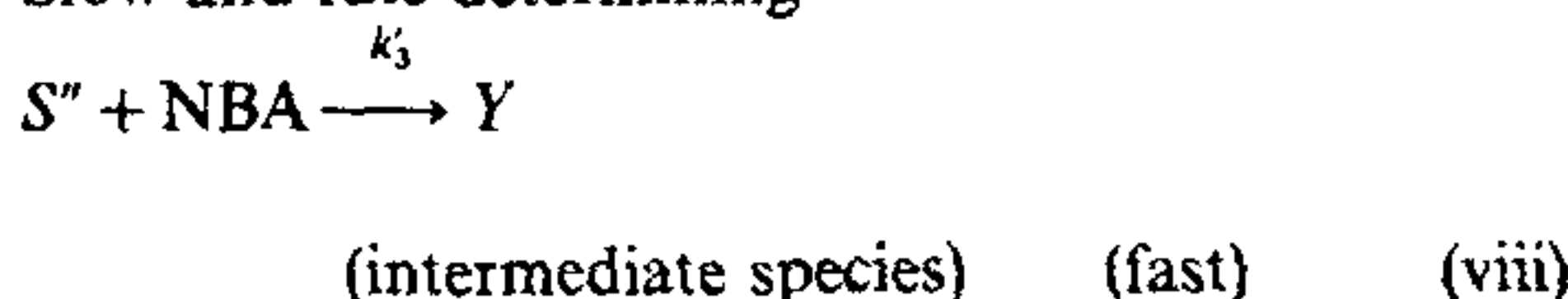
Application of steadystate treatment to S'' yields the rate law (8) as

$$-\frac{d[NBA]}{dt} = k'[S][H^+], \quad (8)$$

where $k' = \left(\dfrac{3k_1k_2}{k_{-1}+k_2}\right).$

Both mechanistic schemes proposed with protonated NBA (N$^+$BAH) and NBA itself as oxidant yield rate laws (7 and 8) which conform to experimental results. However, step (v) in scheme 1 involving interaction betweeen similarly charged ions has been assumed to be fast step which does not appear to be very reasonable. It is therefore concluded that the reaction proceeds with mechanistic scheme 2.

A negative dielectric effect and insignificant influence of ionic strength support the contention that the enolic form of ketone controls the rate of the reaction as indicated in step (vii).

The proposed mechanism is also supported by the magnitude of the solvent isotope effect. A preequilibrium fast proton transfer with specific acid catalysed reaction is indicated by the higher rate value in deuterium oxide (D$_2$O). It is reported in literature that for any proton catalysed reaction, one should expect a solvent isotope effect[8] (kD_2O/kH_2O) of about 2-2.5. A value of $kD_2O/kH_2O = 2.1$ has been found for the rate of acid-catalysed enolisation of acetone[9]. In the present case a solvent isotope effect corresponding to

$k_0 D_2 O k_0 H_2 O = 1.8-2.05$ at $35°$ and $1.86-2.12$ at $40°$ has been obtained in $40-80°_0 D_2 O$, respectively. Thus the observed solvent isotope effect accords well with the reported values and further establishes that the enol form of acetone is the proper route of this particular redox process.

9 October 1984; Revised 14 December 1984

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NEWS

THE INTERNATIONAL NUCLEAR SAFETY ADVISORY GROUP [INSAG]

Vienna, 14 March 1985.—The international Nuclear Safety Advisory Group (INSAG) met for the first time at the Headquarters of the International Atomic Energy Agency from 11–13 March, 1985. This group is composed of 13 eminent experts from nuclear safety licensing authorities, nuclear industry and safety research and development of OECD, CMEA and developing countries.

The Director General of the IAEA in opening the meeting stressed that the group will provide a forum for exchange of significant information in the field of nuclear safety and will help to identify important current safety issues. However, it will neither formulate safety standards nor carry out any regulatory activities. The members of INSAG presented specific highlights of the nuclear safety trends in their countries from the regulatory, industry and research point of view. Several issues with important safety implications and for which advice from INSAG could provide practical value to the nuclear community were identified during the following discussion. The group selected among them three issues, source term, incident feedback and human element as first items for further work. A large number of experts from all over the world took part in the activities in this meeting.

The next meeting for the group is scheduled for 7–9 October 1985. (IAEA, PR 85/6, International Atomic Energy Agency, Wagramerstrasse 5, P.O. Box 100, A-1400, Vienna, Austria).