

Inhibition of Oxidative Nitrogen Fixation in Ultrasonic Field by Volatile Substances

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The cause of the oxidation reactions in the ultrasonic field is still a disputed problem. However, it is general to consider cavitation a precondition for the reactions. In this connection attention is drawn to the action of substances inhibiting oxidation reactions. According to Bresler¹ the oxidation reactions are generally inhibited by the effect of substances with a high vapour pressure (of the order of 1 atm.). The inhibition could then be explained by assuming that the substances with a high vapour pressure are distilled from the aqueous solution to the cavitation bubble causing therein so high a gas pressure that electric discharges cannot take place within the bubble. In this way he explains *e. g.* the inhibitory effect of ammonia and ether on the oxidation phenomena.

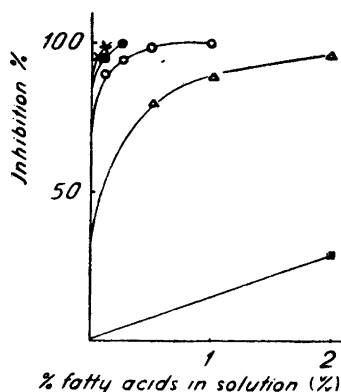
In the present work a study is made on the inhibitory effect of different volatile substances on nitrogen fixation in the ultrasonic field. The aim of the work is to throw light on the manner of effect of these inhibitors.

METHODS

Ultrasonic vibrations were produced as described previously². Since the earlier studies had revealed that in a strongly acid solution (pH 1-2) chiefly nitrate is formed and in a slightly acid or alkaline solution chiefly nitrite, the experiments were made at about pH 6.5. However, when volatile fatty acids were used the pH was lower (pH 3-6), depending on the amount and dissociation of fatty acid. Nitrogen fixation in our experimental conditions could be followed by nitrite determinations³ although some nitrate-N was formed. In higher concentrations of fatty acid nitrite determination no longer gives a correct picture of the N-fixation but this has no essential significance since the low concentrations of inhibitors are the most important.

Fig. 1. Inhibitory effect of volatile fatty acids on nitrogen fixation.

□ Acetic acid Δ Propionic acid
 ○ Butyric acid ● *I s o*-valeric acid
 × Caproic acid



EXPERIMENTS AND RESULTS

100 ml of the test solution were used in the experiments and free access of air was allowed to the test cylinder. The temperature of the solution was maintained at about 20°C by means of cold water passing through the solution in a coil-shaped tube. The inhibition was calculated as per cent of nitrite nitrogen in the solution without added inhibitors. The reaction time was 10 min, except in experiments with methylaniline and aniline, when it was 5 min. Figures 1—5 show the inhibitory effect on N-fixation by volatile fatty acids (1), alcohols (2), aldehydes (3), aniline and methylaniline (4), and benzene, toluene and xylene (5).

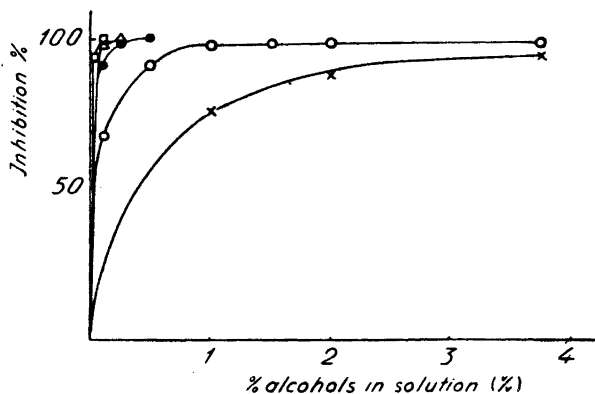


Fig. 2. Inhibitory effect of different alcohols.

× Methylalcohol ○ Ethylalcohol ● Propylalcohol
 Δ *n*-Butyl alcohol □ *I s o*-amylalcohol

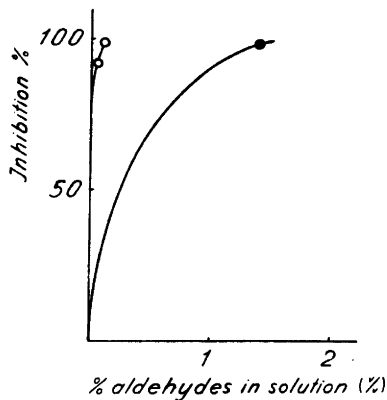


Fig. 3. Inhibitory effect of aldehydes.

○ Acetaldehyde ● Formaldehyde

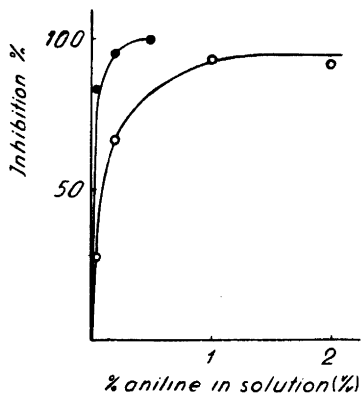


Fig. 4. Inhibitory effect of aniline and methylaniline.

● Methylaniline ○ Aniline

With respect to the inhibitory effect of fatty acids it is noteworthy that in the presence of propionic acid nitrite was formed within the first 5 min but afterwards it decreased, disappearing entirely after 10 min (Fig. 6). An abundance of hydrogen peroxide was then present in the solution.

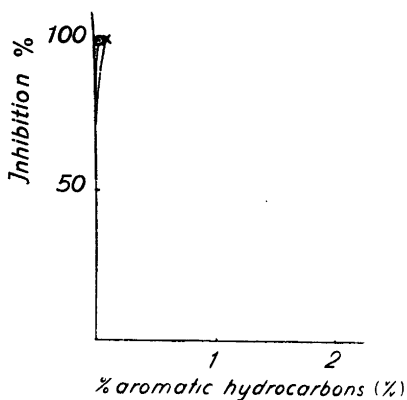


Fig. 5. Inhibitory effect of benzene, toluene, and xylene.

○ Benzene
● Toluene
× Xylene

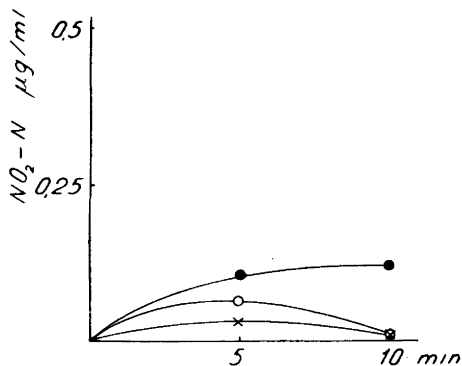


Fig. 6. Formation and disappearance of nitrite at different concentrations of propionic acid.

○ 0.5% (v/v) propionic acid
● 1% (v/v) propionic acid
× 2% (v/v) propionic acid

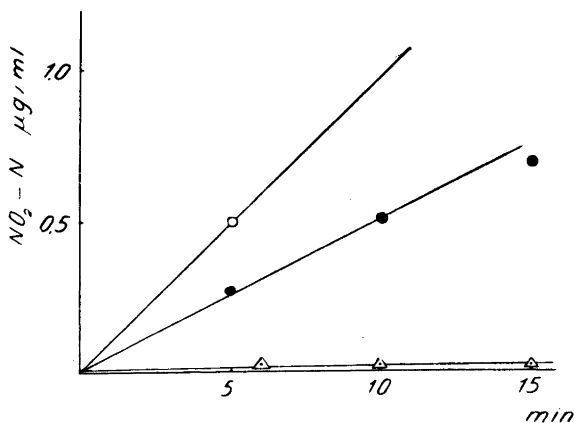


Fig. 7. Nitrite formation in solution of *iso*-valeric acid at pH abt. 5 and 11.5, in butyl alcohol at pH abt. 6.5 and 10.

- distilled water
- 0.25 % (v/v) *iso*-valeric acid neutralized to pH 11.5
- △ 0.25 % (v/v) butyl alcohol, pH 10
- 0.25 % (v/v) *iso*-valeric acid, not neutralized

If the fatty acids are neutralized they lose a great part of their inhibitory effect. Fig. 7 shows nitrite formation in 0.25 % solution of *iso*-valeric acid which was neutralized with NaOH to pH 11.5. It can be seen from the same figure that the formation of nitrite was completely inhibited in a corresponding solution of *iso*-valeric acid which was not neutralized. Butyl alcohol completely prevented nitrite formation in a solution made alkaline with NaOH as well as in a pure water solution without NaOH.

DISCUSSION

The results reported on the inhibitory effect of volatile substances on the nitrogen fixation in the ultrasonic field show that the inhibition grows with the increase in the volatility which in the homologous series takes place up to a certain limit with the lengthening of the carbon chain.

The volatilities with steam of the examined substances from dilute solutions are presented in Tables 1 and 2.

In vacuo, at a pressure of about 15 mm the distillation of acetic, propionic, and butyric acids is somewhat lower than at ordinary pressure, but still of the same order. The distillation constant of propionic acid from dilute water solution is *in vacuo* about 1, hence, vapour removed from 1 % solution of propionic acid contains 1 % propionic acid and 99 % water.

Table 1. Distillation constants of some volatile fatty acids (dilute water solutions).

Fatty acids	Concentration	Distillation constant	Half-distillation value
	%	<i>k</i>	%
Acetic acid ⁴	0.09	0.657	36.6
	0.51	0.657	36.6
	1.90	0.660	36.7
Propionic acid ⁴	0.07	1.235	57.5
	0.13	1.239	57.6
	1.32	1.270	58.5
Butyric acid ⁴	0.05	1.92	73.5
	0.16	1.96	74.4
	0.88	2.00	75.0
	2.29	2.02	75.3
<i>n</i> -Valeric acid ⁴		2.50	82.4
<i>iso</i> -Valeric acid ⁵		3.27	89.6
Caproic acid ⁵		3.08	88.2

Table 2. Distillation constants of some alcohols, aldehydes and anilines (dilute water solutions).

Alcohols	Concentration	Distillation constant	Half-distillation value
	%	<i>k</i>	%
Methylalcohol ⁴	0.05	8.9	99.8
Ethylalcohol ⁴	0.10	12.9	~100
<i>Aldehydes</i>			
Formaldehyde ⁴	0.09	2.6	83.0
Acetaldehyde ⁴	0.04	>40	~100
<i>Anilines</i>			
Aniline ⁴	0.05	5.5	98
Methylaniline ⁴	0.03	~16	~100

In the light of our results the conclusion that the inhibitory effect of the volatile substances is due to their distillation to the cavitation bubbles does not explain the phenomenon. If we examine our results obtained with different fatty acids we can note that propionic acid in a 0.5 % solution will inhibit nitrogen fixation by as much as 80 %, yet the steam evaporating from such a solution *in vacuo* contains only about 0.5 % propionic acid (Table 1). In 0.1 % butyric

acid solution the inhibition is 90 %, the steam containing only 0.14 % butyric acid. The vapour pressure of propionic acid and butyric acid is so small that we do not consider their inhibitory effect explicable by Bresler's idea that a high gas pressure inside the cavitation bubble prevents electric discharges therein.

On the other hand, the effect of the examined substances on the surface tension seems to deserve serious consideration as an explanation for the observed inhibition. The inhibitory effects of the substances used have been the greater, the more they have lowered the surface tension of the solution. The probable dependence of the energetic state of cavitation on the surface tension may be the cause of the inhibition of the oxidative N-fixation in our experiments.

In fatty acid solution made alkaline (experiment with *iso*-valeric acid on p. 664) inhibition of nitrogen fixation is slight. This can be explained by assuming that the alkali salts of fatty acids lower the surface tension less than do the corresponding free acids ⁶. It can also be assumed that lowering of the surface tension takes place at a slower rate in the alkali salt solution than in the corresponding solutions of free acids. The duration of the cavitation bubble in the US field is of the order of 10^{-6} sec. The time being so brief, the surface tension is dynamic yet decreased in low-molecular fatty acid solutions and corresponding alcohol solutions. In soap solutions (observations with Na-oleate solution ⁶) decrease in the dynamic surface tension is slower, and therefore, no change occurs in 10^{-6} sec.

We have not yet examined to what extent the volatile substances possibly are oxidized by the effect of ultrasonics. The observation made by us that nitrite is at first more abundantly formed at low propionic acid concentrations and that it is greatly decreased with prolonged reaction time, suggests participation of propionic acid in some way in the oxidation reaction in the ultrasonic field. Prudhomme and Grabar ⁷ have found that the benzene ring is oxidized in the ultrasonic field, hence, the strong inhibitory effect of aromatic hydrocarbons on nitrogen fixation could possibly be due to this (competition between nitrogen and aromatic hydrocarbons).

Breuning ⁸ has reported that nitrite is formed in an ultrasonic field, which is brought about with so small energies that cavitation is considered impossible. Accordingly, formation of nitrite would not be associated with the reactions taking place in the cavitation bubble but would proceed along quite different lines. There is, however, no confirmation to this observation.

SUMMARY

Inhibition of nitrogen fixation in the ultrasonic field by certain organic volatile substances of homologous series has been examined. The organic substances belonged to aliphatic fatty acids, aldehydes, alcohols, aromatic hydrocarbons, and amines which were used in 0.05–2 % solution. The reaction took place in water solutions at pH about 6.5, in fatty acid solutions at pH 3–6.

On the basis of the results the cause of inhibition is discussed. The most likely reason suggested is the influence of the volatile substances on the surface activity and the resultant energetic changes in the cavitation. Distillation of substances into the cavitation bubbles has not been regarded as sufficient explanation.

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