Studies of N-Halogeno-compounds. Part VI. The Kinetics of Chlorination of Tertiary Amines.*

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From kinetic and spectroscopic evidence the main chlorinating agent in the interaction of hypochlorous acid and trimethylamine in aqueous solution is the trimethylchlorammonium ion Me_3NCl^+ (Bohme and Krause, *Ber.*, 1951, **84**, 170). The products (cf. Crane, Forrest, Stephenson, and Waters, *J.*, 1946, 827) are dimethylchloramine and formaldehyde. Similar kinetics are observed in the chlorination of triethylamine. With tertiary amines present in excess it is found that chlorine in a solution of hydrochloric acid, present to prevent hydrolysis of the chlorine, is much less effective as a chlorinating agent than hypochlorous acid at the same pH, owing to the displacement of the equilibrium $R_3NCl^+ + Cl^- \rightleftharpoons Cl_2 + R_3N$.

A COMPREHENSIVE study was made by Waters and his co-workers (*loc. cit.*) of the products of the reaction of molecular chlorine, aqueous bleaching powder, and *N*-chloroimides on various tertiary amines. They concluded that the first and slowest step was the substitution by chlorine of a hydrogen atom attached to an α-carbon atom of the amine. The α-halogenated tertiary amine rapidly decomposed to give an aldehyde and a secondary amine. With aqueous bleaching powder solution the secondary amine reacted to give the dialkylchloramine instead of being precipitated as the hydrochloride as in organic solvents. The present work has been confined to the kinetics of interaction in aqueous solution and in particular the interaction of trimethyl- and triethyl-amine with aqueous hypochlorous acid and chlorine.

With tertiary amines and halogens in carbon tetrachloride simple addition occurs to give crystalline salts of the type $[R_3NX^+]X^-$ which have been isolated by Bohme and Krause (*Ber.*, 1951, **84**, 170) (cf. Hantzsch and Graf, *ibid.*, 1905, **38**, 2154). In view of the reactivity of the analogous dialkylchlorammonium ions, R_2NHCl^+, which account for the interaction of diethylchloramine and phenols (Brown and Soper, *J.*, 1953, 3576), it was thought possible that the trialkylchlorammonium ion might play a part in the chlorination of the tertiary amine.

EXPERIMENTAL

The chlorine complex with trimethylamine was prepared by the method of Bohme and Krause (*loc. cit.*) by mixing the two reactants in carbon tetrachloride solution at −15°. The crystalline product was of 95% purity calculated on the iodine titre. When dry, the complex was quite stable over an examined period of 3—4 days in a darkened desiccator.

Absorption Spectra of Aqueous Trimethylchlorammonium Chloride Solutions.—The absorption curves of monochloramines, dichloramines, and nitrogen trichloride were determined by Metcalf (*J.*, 1942, 148). All have absorption maxima within the range 245—340 mμ, whilst hypochlorous acid has an absorption maximum at 235, and the hypochlorite ion (Corbett, Metcalf, and Soper, *J.*, 1953, 1927) at 295 mμ. A neutral aqueous solution of trimethylchlorammonium chloride gave the absorption spectrum of dimethylchloramine almost immediately, but in acid solutions the appearance of the dimethylchloramine was delayed. The chlorammonium chloride gave no absorption in the 220—350 mμ range, showing the absence of free chlorine or hypochlorous acid, and little change in the absorption is observable in 0·01N-sulphuric acid during 30 min. Typical absorption curves are shown in Fig. 1.

Freezing Point of Aqueous Trimethylchlorammonium Chloride.—Since in 0·01N-sulphuric acid only 3% decomposition of the complex occurs in 30 min., it is possible to examine the freezing point of solutions of the complex in acid of this concentration which itself freezes at −0·015°. A solution of 0·196M-complex of 95% purity froze at −0·780°, a lowering of 0·765° corresponding to a molarity of 0·765/1·86 = 0·41M. The high value for the freezing-point depression is in conformity with Bohme and Krause's formulation of the complex as $[R_3NCl]^+Cl^-$. The absorption curve is therefore attributed to presence of the R_3NCl^+ ion.

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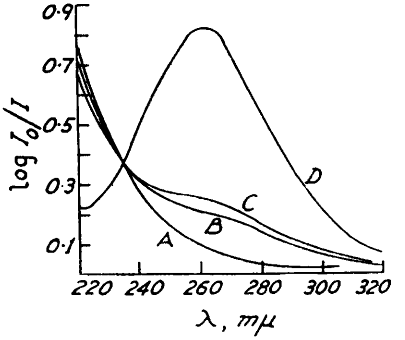
* Part V, *J.*, 1953, 3576.

Formation of Trimethylchlorammonium Hydroxide.—When the absorption spectrum of a solution buffered at pH 2·6 (phosphate buffer) containing equal parts of 0·01M-trimethylamine sulphate and hypochlorous acid was determined immediately after mixing, it was found to be identical with that of the trimethylchlorammonium chloride. At pH 2·6, the conversion of the mixture into dimethylchloramine is fairly slow and the curve could be obtained before 5% conversion occurred (Fig. 2). At higher pH's rapid conversion into dimethylchloramine occurred, but the curve of the trimethylchlorammonium ion appears first. There can be little doubt that on mixing trimethylamine and hypochlorous acid there is a rapid formation of the chloroammonium hydroxide, except in acid solutions such as 0·1N-sulphuric acid where the hypochlorous acid spectrum persists for over 30 min.

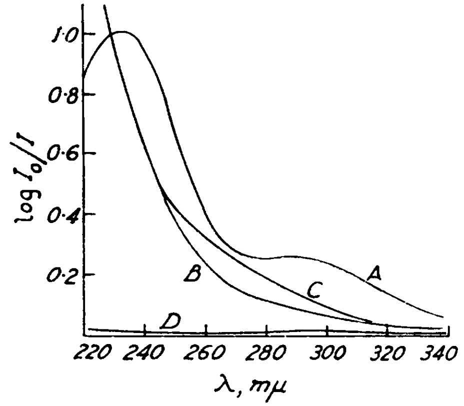
Formation of Triethylchlorammonium Hydroxide.—In contrast with the behaviour of trimethylamine, in mixtures of trimethylamine and hypochlorous acid at pH 2·8 there was little formation of the triethylchlorammonium ion within 1 hr., but in more alkaline solution, *e.g.*, pH 3·4, the characteristic absorption of this acid was replaced within 30 min. by that of the chlorammonium ion. At equal pH's the triethylchlorammonium complex in general is not formed as rapidly as the trimethylchlorammonium complex. An attempt to prepare $[Et_3Cl]^+Cl^-$ by using Bohme and Krause's method for $[Me_3Cl^+]Cl^-$ (*loc. cit.*) did not yield a stable compound, rapid decomposition to chloramines and aldehydes occurring.

FIG. 1. *Absorption curves of* $Me_3NCl^+Cl^-$.



A, Immediately after solution in phosphate buffer pH 2·8.
B, After 40 min. at pH 2·8.
C, After 1 hour at pH 2·8.
D, After 30 min. at pH 6·0 (dimethylchloramine).

FIG. 2. *Absorption curves of* HOCl *and* NMe_3.



A, 0·01M-HOCl in phosphate buffer pH 2·6.
B, 0·01M-HOCl and 0·01M-$(Me_3NH)_2SO_4$ at pH 2·6 immediately after mixing.
C, As *B*, but after 20 min.
D, 0·01M-$(Me_3NH)_2SO_4$ at pH 2·6.

Products of the Reaction between Trimethylamine and Hypochlorous Acid.—The reaction $(CH_3)_3N + 2HOCl = (CH_3)_2NCl + H{\cdot}CHO + HCl$ requires that the loss in total oxidising power of the solution should parallel the increase in chloramine titre. The increase in the latter can be obtained by first removing the free hypochlorous acid with phenol under conditions which will leave the chloramine unaffected. That this condition is fulfilled is shown in Fig. 3, where the total oxidising power of the solution measured after treatment with potassium iodide is compared with the titre of the chloramine formed. The formaldehyde present at the end of a reaction was determined by removal of the chloramine and any residual hypochlorous acid by potassium iodide, the liberated iodine being precisely removed by sodium thiosulphate. The formaldehyde was then estimated by the bisulphite method, excess of sodium hydrogen sulphite being added and, after 45 min. to ensure complete formation of the addition compound, the uncombined bisulphite being estimated iodometrically. On use of 60 c.c. of 0·578N-hypochlorous acid (0·01783 mole of HOCl) and 0·05 mole of trimethylamine, the formaldehyde found was 0·00855 mole, corresponding to a 49·2% yield calculated on the initial hypochlorous acid. Analyses by the dimedone method gave a corresponding percentage yield of formaldehyde of 49%.

Kinetics of the Reaction.—In the examination of the effects of pH, and the concentrations of tertiary amine and hypochlorous acid at 25·00° ± 0·02° and constant ionic strength, the reaction rate was evaluated as an initial velocity, v_0, obtained either from the initial slope of the curve obtained by plotting total titre against time or from the curve obtained by plotting the titre of dialkylchloramine produced against time (Fig. 3). These were the same within experimental error. With a constant concentration of trimethylamine of 0·01M at pH 3·40 (succinate buffer) and 0·2M-potassium nitrate present to maintain an approximately constant ionic strength, the following results were obtained for v_0 (moles l.$^{-1}$ min.$^{-1}$) in a series of runs with varying initial concentrations of hypochlorous acid :

$[HOCl]_0 \times 10^3$	0·45	1·13	1·28	2·05	2·26	3·10	4·80	6·43	8·80	9·48	14·20
$v_0 \times 10^4$	0·17	0·37	0·45	0·67	0·73	0·84	1·02	0·94	0·51	0·25	0·11

On gradual increase of [HOCl], the reaction velocity passes through a maximum at a ratio of [HOCl] to [amine] of approximately 1 : 0·5.

With a constant concentration of hypochlorous acid of 0·0024M and similar conditions of pH and ionic strength as in the above series but with varying initial concentrations of trimethylamine, added in the form of standard sulphate solution, the values of v_0 were found to be proportional to the excess concentration of amine over that of the hypochlorous acid :

$[Me_3N]_0 \times 10^3$	3·00	5·00	6·50	8·10	10·00
$([Me_3N]_0 - [HOCl]_0) \times 10^3$	0·60	2·60	4·10	5·60	7·60
$v_0 \times 10^4$	0·06	0·25	0·41	0·52	0·73

These experiments, together with those demonstrating the rapid formation of the trimethylchlorammonium ion from trimethylamine and hypochlorous acid, indicate that the reaction rate is proportional to the product of concentrations of chlorammonium ion and the uncombined amine :

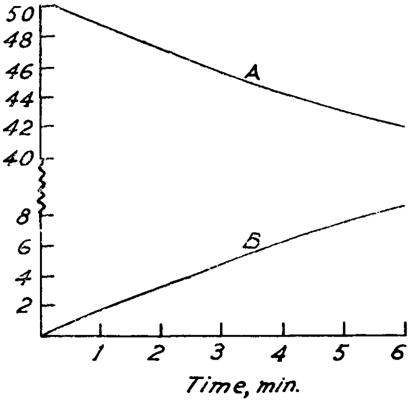


FIG. 3. *Production of* Me_2NCl: Me_3N = 0·01M; HOCl = 0·00503M; pH 3·58.
A, Fall in oxidising titre of solution.
B, Production of Me_2NCl.

$$Me_3N + HOCl \xrightarrow{\text{Fast}} Me_3NCl^+OH^-$$

$$Me_3NCl^+ + Me_3N \xrightarrow{\text{Slow}} \text{Products} \xrightarrow{H_2O} Me_3NH^+ + Me_2NH + H{\cdot}CHO$$

$$Me_3NCl^+ + Me_2NH \xrightarrow{\text{Fast}} Me_3NH^+ + Me_2NCl$$

Kinetic equation. Over the acid range pH 3—4 where rates are convenient to measure, the excess of amine is present almost entirely in the form of its cation whilst [free amine] = $[OH^-]$[excess of amine]$/K_b$, K_b being the classical basic ionisation constant of trimethylamine. If the initial concentration of excess of amine = ([total amine]$_0$ — $[HOCl]_0$) = $[Me_3NH^+] = a$ and of chlorammonium ion $[Me_3NCl^+] = [HOCl]_0 = b$, then at time t when $[Me_2NCl] = x$, $[Me_3NH^+] = a + x$ and $[Me_3NCl^+] = b - 2x$. If a constant $k_{2(\text{obs.})}$ is defined by $v = k_{2(\text{obs.})}$[excess of amine]$[Me_3NCl^+]$, $k_{2(\text{obs.})} = [2{\cdot}303/t(2a + b)] \log b(a + x)/a(b - 2x)$ for any one reaction at constant pH. If the kinetics involve free amine rather than amine cation, $v = k_2[Me_3N][Me_3NCl^+]$ and $k_{2(\text{obs.})} = k_2[Me_3N]/[Me_3NH^+]$, whence $k_{2(\text{obs.})}[H^+] = k_2K_w/K_b$. In this event, the product of $k_{2(\text{obs.})}$ and the hydrogen-ion concentration should be constant.

At pH 3·69 and $[Me_3N]_0$ = 0·0100, $[HOCl]_0$ = 0·00490, the following results illustrate the satisfactory nature of the rate equation for $k_{2(\text{obs.})}$, the titres marked * representing total oxidising power of the solution, and the other titres being that of dimethylchloramine formed :

Time, min.	0	0·75	2·0	3·0	3·67	4·25	4·83	5·58
Titre (c.c. of 0·02N-$Na_2S_2O_3$) of 10 c.c.	49·00*	1·60	4·20	6·12	7·35	8·33	9·20	39·80*
$k_{2\,(\text{obs.})}$	—	8·70	8·75	8·85	8·8	8·8	8·75	—

Experiments on the variation of $k_{2(\text{obs.})}$ with pH showed that in the range pH 3—4 the rate is proportional, as in the interaction of hypochlorous acid and dialkylamines, to the hydroxyl-ion concentration of the buffered solution. This indicates that the reaction rate involves the free amine base as opposed to the amine cation. With initial concentrations of trimethylamine of 1·00 × 10^{-3}M and hypochlorous acid of 0·50 × 10^{-3}M, the initial rate, v_0, and the rate constants $k_{2(\text{obs.})}$ for the reactions in the acid range varied as follows :

pH	3·04	3·37	3·58	3·69	3·97	5·0—12·0
$v_0 \times 10^4$	0·45	1·05	1·5	2·1	4·0	Very fast
$k_{2(\text{obs.})}$	1·98	4·15	6·46	8·81	16·6	—
$k_{2(\text{obs.})} \times [\text{H}^+]$	17·2	17·7	17·0	17·9	17·8 × 10^{-4}	—

The rate in more alkaline solutions decreases and becomes measurable above pH 12. This is probably due to the displacement of the equilibrium $\text{Me}_3\text{NCl}^+ + \text{OH}^- \longrightarrow \text{Me}_3\text{N} + \text{HOCl}$ and the conversion of HOCl into OCl^-, resulting in removal of the chlorammonium ion from the system. The values of v_0 with concentrations as above and $[\text{OH}^-]$ equal to 0·025, 0·05, 0·10, and 0·20 are respectively 9·5, 3·0, 0·89, and 0·46 × 10^{-4} for solutions in which sodium hydroxide is present. These systems in strongly alkaline solution are too unstable for very accurate measurement.

With a constant initial concentration of 0·0100M-trimethylamine added as sulphate and varying initial concentrations of hypochlorous acid, mean values for $k_{2(\text{obs.})}$ at pH 3·40 for several experiments are given below :

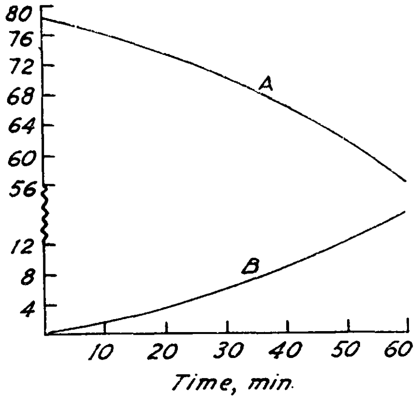


FIG. 4. Et_3N = 0·01M; HOCl = 0·00794M; pH 3·40, *showing autocatalysis.*

A, Total titre.
B, :NCl titre.

[HOCl] × 10^3	0·45	1·13	2·26	3·10	4·81	6·43	8·80	9·48
$k_{2(\text{obs.})}$	4·10	4·16	4·36	4·30	4·44	4·50	4·76	4·84

Within each experiment the individual values of $k_{2(\text{obs.})}$ were reasonably constant. However, $k_{2(\text{obs.})}$ tends to increase gradually when the hypochlorous acid concentration approaches that of the amine and, owing to formation of the chlorammonium ion, the concentration of free amine becomes low. Under these conditions the autodecomposition of the chlorammonium cation itself would result in higher values for $k_{2(\text{obs.})}$ at low concentrations of free amine.

Results with Triethylamine.—Although the rate of reaction of hypochlorous acid with triethylamine shows the same general dependence on the excess of amine over that of the hypochlorous acid and also on the alkalinity of the solution, the kinetic results are complicated by the fact that the triethylchlorammonium ion is not formed rapidly and quantitatively in the pH range studied, as shown from the ultra-violet absorption curves. The chlorammonium salt is formed more rapidly in the less acidic solution. The consecutive reactions $\text{HOCl} + \text{Et}_3\text{N} \longrightarrow \text{Et}_3\text{NCl}^+ + \text{Cl}^-$; $\text{Et}_3\text{NCl}^+ + \text{Et}_3\text{N} \longrightarrow$ Products, thus overlap, and the rate of chlorination and of production of Et_2NCl both show evidence of autocatalysis (Fig. 4). The relation of the initial rate of production of diethylchloramine, v_0, to increasing initial concentration of hypochlorous acid and a fixed concentration of triethylamine = 10^{-2}M at pH 3·40 is given below :

[HOCl] × 10^3	1·07	2·69	4·96	7·94	8·24	10·8	15·3	20·6	30·0
$v_0 \times 10^4$	0·07	0·12	0·14	0·15	0·14	0·13	0·11	0·07	0·01

This rate is approximately 0·65 times that of the rate of total loss of oxidising power by the solution but diminishes as the ratio of hypochlorous acid to triethylamine increases. With trimethylamine the rate of formation of dialkylchloramine equals the total loss of oxidising power of the solution. Whereas with trimethylamine a maximum rate was observed when the initial concentration of hypochlorous acid is half that of the amine, yet the maximum initial rate with triethylamine instead of occurring at this point, *viz.*, 5×10^{-3}M, appears at a higher concentration of hypochlorous acid. This is due to the greater relative time required to form the chlorammonium ion, and to its formation being assisted by higher concentrations of hypochlorous acid.

The Relative Chlorinating Efficiencies of the Chlorammonium Ion and Chlorine.—When to a series of mixtures of 10^{-2}M-trimethylamine and $0·5 \times 10^{-2}$N-hypochlorous acid at pH 2·45 increasing amounts of potassium chloride were added, the yellow colour and odour of chlorine developed, and the reaction rate diminished as set out below, potassium nitrate being present to maintain constant ionic strength :

KCl, N	0·00	0·09	0·18	0·45	0·90	1·35	1·80
KNO_3, N	1·80	1·71	1·62	1·35	0·90	0·45	0·00
$v_0 \times 10^4$	2·35	2·25	2·20	1·95	1·40	1·10	0·90

Spectrophotometric examination of the mixture containing 1·80M-potassium chloride showed first the formation of the chlorammonium ion on mixing of the amine and hypochlorous acid, and then the production of chlorine on addition of potassium chloride. Evidently a reversible equilibrium exists, $R_3NCl^+ + Cl^- \rightleftharpoons R_3N + Cl_2$. Comparison of the spectra with those of standard solutions of chlorine showed that the addition of 1·80N-potassium chloride resulted in approximately 60% of the active chlorine being present as chlorine.

Since the remainder of the active chlorine, *i.e.*, 40%, is in the form of chlorammonium ion, the reduction in the reaction rate from 2·35 to 0·90 is paralleled by the reduction in the amount of the rate-determining chlorammonium ion. One explanation of this result is that the Me_3NCl^+ ion is a much more effective chlorinating agent than molecular chlorine. The displacement of the equilibrium $R_3NCl^+ + Cl^- \rightleftharpoons R_3N + Cl_2$ in solutions of high chloride concentration explains the anomalous and at first sight puzzling result that with excess of amine present hypochlorous acid is more efficient in reaction with tertiary amines than solutions of chlorine to which chloride is added to prevent chlorine hydrolysis.

DISCUSSION

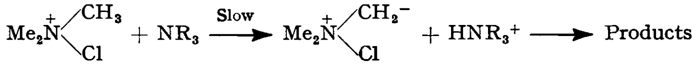
The kinetics indicate clearly that the interaction of hypochlorous acid or chlorine and trimethylamine involves the chlorammonium cation. In mixtures of amine and hypochlorous acid the rate is also dependent on the concentration of free amine base. Whether this base is always a necessary reactant is uncertain, for solutions of the chlorammonium chloride in the absence of added amine also decompose to form the dimethylchloramine at pH 7. Moreover, there is some evidence that the rate, in mixtures of chlorammonium cations and free amine, is not strictly proportional to the free amine concentration except where this concentration is high. At lower concentrations of free amine, a direct decomposition of the chlorammonium ion also appears to be of importance.

There appear to be two reaction possibilities which conform to the observed kinetics. In the first the chlorammonium ions act as a highly efficient electrophilic chlorinating agent, chlorinating alkyl groups in the tertiary amine. If the chlorination is in the α-position, hydrolysis follows with production of the aldehyde and secondary amine, which in the presence of the efficient chlorinating agent is converted very rapidly into the dialkylchloramine. This would require equality of rates of α-chlorination and production of dialkylchloramine if the rate-determining step is α-chlorination. If chlorination at β-carbon atoms also occurs as well as α-chlorination, the rate of carbon chlorination will exceed that of dialkylchloramine formation. It is observed with trimethylamine, where chlorination must be confined to the α-carbon atom, that the two rates are equal whereas in triethylamine the rate of *C*-chlorination as given by the loss of active chlorine in the solution is about 1·5—1·6 times that of the formation of diethylchloramine. The production of other chlorinated products isolated by Waters and his co-workers (*loc. cit.*) would be in harmony with an attack by a halogenating agent on one of the alkyl groups of the tertiary amine.

The alternative explanation is based on Bohme and Krause's suggestion (*loc. cit.*) that the trimethylchlorammonium halide decomposes as follows :

$$[\overset{+}{N}Me_2X\cdot CH_3]\overset{-}{X} \xrightarrow{-XH} \overset{+}{N}Me_2X\cdot\overset{-}{C}H_2 \longrightarrow NMe_2\cdot CH_2X \longrightarrow \overset{+}{N}Me_2H_2\,\overset{-}{X} + H\cdot CHO$$

The dependence of the rate on the free amine concentration may on this view be due to its action as a proton acceptor removing a proton from an α-carbon atom :



$$Me_2\overset{+}{N}{<}^{CH_3}_{Cl} + NR_3 \xrightarrow{\text{Slow}} Me_2\overset{+}{N}{<}^{CH_2^-}_{Cl} + HNR_3^+ \longrightarrow \text{Products}$$

This mechanism of proton removal from the chlorammonium ion would also explain the surprising result that when the chlorammonium ion is partially converted into chlorine by displacement of the equilibrium $R_3NCl^+ + Cl^- \longrightarrow Cl_2 + R_3N$, the reaction is made slower in proportion to the conversion of the chlorammonium ion into chlorine. On the first hypothesis, on the other hand, in order to explain this result one must assume that, in comparison with the chlorammonium ion, chlorine is relatively inactive as a chlorinating agent. This is unlikely in view of the relative ease of the ionisation of chlorine and of the chlorammonium ion into positive chlorine. If K_1 is the equilibrium constant of $Cl_2 \rightleftarrows Cl^+ + Cl^-$ and K_2 that of $Me_3NCl^+ \rightleftarrows Me_3N + Cl^+$, the ratio K_1/K_2 is given by the equilibrium constant of $Me_3N + Cl_2 \rightleftarrows Cl^- + Me_3NCl^+$. The spectroscopic determination of the free chlorine in solutions of the chlorammonium ion in the presence of 1·8N-potassium chloride gives a value for this equilibrium constant of approximately $1{\cdot}5 \times 10^2$. Although this figure refers to the solvated ions, it would be expected that a chlorine would form positive chlorine at the seat of the reaction, if not more easily than, at least as easily as, the trimethylchlorammonium ion. This would indicate that the hypothesis of direct chlorination as the rate-determining step in dealkylation is unlikely. Further work on the relative efficiencies of chlorine and the chlorammonium ion is proceeding.

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