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Reaction of N-Haloamide. XV.[1] Reaction of Tetrahydrofuran with N,N-Dibromobenzenesulfonamide. (2).[2] Kinetics and Mechanism[3]

Yoshiko Kamiya and Shoji Takemura

Faculty of Pharmaceutical Sciences, Kinki University[4]

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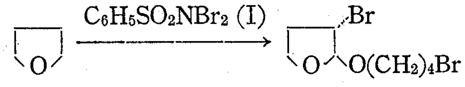
Kinetic studies were made on the reaction of tetrahydrofuran (II) with N,N-dibromobenzenesulfonamide (I) and from the results, the reaction mechanism was proposed.

Results on the first stage of the reaction, namely liberation of bromine can be explained by Eq. (2)—(4). I, which is excited by visible light, acts as a sensitizer. It seems that bromine is liberated from I and simultaneously a ylid-like oxonium ion (III) may be formed as a reactive intermediate.

Results on the second stage, namely consumption of bromine can be explained by Eq. (9)—(16). The mechanism was found to involve chain processes starting with formation of an oxonium ion (IV) from III, and reaction of IV with bromine.

In previous papers on the reactions of N-haloamide with various substances, we reported that N,N-dibromobenzenesulfonamide (I) reacted with ethers under mild conditions: aliphatic ethers[5] gave the corresponding aldehydes and alkyl bromides, and tetrahydrofuran (II)[2] gave *trans*-2-(4'-bromobutoxy)-3-bromotetrahydrofuran.

$$RCH_2OCH_2R' \xrightarrow{C_6H_5SO_2NBr_2\ (I)} RCHO + R'CH_2Br$$



II

It seemed interesting to investigate the mechanism of the latter reaction. The reaction apparently involved two stages (Fig. 1). In the first stage, the theoretical amount of bromine was liberated from I by contact with ether. After the liberation of bromine terminated, the next stage, rapid consumption of the bromine, started spontaneously, *i.e.*, the second stage did not start before the termination of the first stage. The fact was confirmed further by following experiment; addition of I into the reaction mixture of the second stage caused again an increase of bromine, the velocity of bromine liberation was as well as that of first stage and the consumption of bromine did not occur untill theoretical amount of bromine liberated completely. This suggests that I plays a role of quencher for the initiation of the second stage, photolysis of bromine.

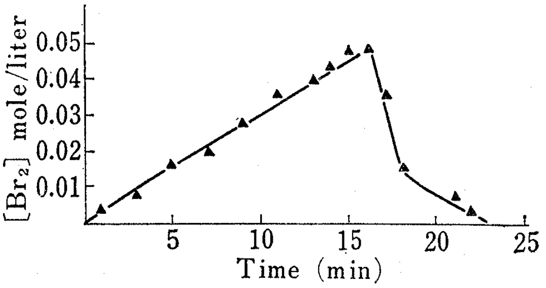


Fig. 1. Change in Concentration of Bromine during the Reaction

Bromine was measured colorimetrically.
reaction conditions
$[I]_0$: 0.05 mole/l CH_2Ci_2
$[II]_0$: 0.1 mole/l CH_2Cl_2
Irradiation from fluorescent light
at 27°

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[1] Part XIV: H. Terauchi, T. Irino, and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), **20**, 1821 (1972).

[2] Part (1): Y. Kamiya (née Ando), S. Takemura, and Y. Ueno, *Chem. Pharm. Bull.* (Tokyo), **17**, 520 (1969).

[3] Part of this work has been published: Y. Kamiya and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), **18**, 848 (1970).

[4] Location: *321 Kowakae, Higashiosaka, Osaka.*

[5] S. Takemura, Y. Ando, H. Terauchi, and Y. Ueno, *Chem. Pharm. Bull.* (Tokyo), **15**, 1331 (1967).

In practice the two stages were able to be measured separately, so we studied the kinetics of the individual stages in the reaction of I with II.

Experimental

Materials——N,N-Dibromobenzenesulfonamide (I): I (mp 113—114°) was prepared as described previously.[6]

Tetrahydrofuran (II): II was dried over $CaCl_2$ and purified by refluxing over $FeSO_4$, followed by distillation from Na. The purified material was stored in the dark. It was filtered through an alumina column (60 g of alumina per 500 ml of II) before use.

Dichloromethane: Commercial CH_2Cl_2 was dried over P_2O_5, purified by distillation and stored in the dark. It was also filtered through an alumina column before use.

General Equipment——Reactor: A three necked flask, equiped with a condenser and an inlet tube for bubbling nitrogen through the reaction. Reactions were carried out at various constant temperatures and intensities of illumination, bubbling the mixtures with nitrogen gas. Other equipments used were a Toshiba FCL 30D/NL fluorescent lamp, a Toshiba SOI-5 photometer with photovolatic cell and a Hitachi 101 spectrophotometer.

Relationship between Absorbance and Titration——Standard solutions of various concentrations of bromine in CH_2Cl_2 were prepared. The concentration of each solution was measured iodometrically and the absorbance of each solution was determined colorimetrically at 415 mμ. The absorbances were proportional to the values obtained iodometrically.

Kinetic Mesurements——First Stage: I was allowed to react with II in CH_2Cl_2 in the reactor. Samples of the reaction mixture were withdrawn at intervals and their bromine concentration was measured colorimetrically. Fig. 1 shows a plot of the molar concentration of bromine against the time of reaction. In every reactions, the values increased linearly to a peak of bromine concentration, $[Br_2]$. Therefore, the rate of the first stage of the reaction, $d[Br_2]/dt$, was able to be measured directly as the slope of the line. The rate of the first stage was measured under various conditions, (*i.e.* at various temperatures, initial concentrations of I and II, $[I]_0$ and $[II]_0$, and intensities of illumination).

Second Stage: The rate of the second stage was too large under the same conditions of illumination as in the first stage. So illumination on the second stage was controlled to 250 lux and then the decrease of bromine was measured colorimetrically at regular intervals. The effects of $[Br_2]$ and [II] on the rate of the second stage were studied.

Result and Discussion

(1) First Stage

Dependence of Temperature——The reaction rate was measured in the range of 25° to 43° under the constant of $[I]_0$, $[II]_0$, and the intensity of illumination. An Arrhenius Plot (Fig. 2) shows that the rate was slightly dependent on temperature.

Effect of the Concentration of N,N-Dibromobenzenesulfonamide——Fig. 1 shows evidently that the rate was independent of [I]. Furthermore, the influence of [I] on the rate was examined at 40° and 27° under the constant of $[II]_0$ and the intensity of illumination. The results shown in Fig. 3 indicates that the rate was not influenced by [I].

Effect of the Concentration of Tetrahydrofuran——The effect of [II] on the rate is shown in Fig. 4, where $\log(d[Br_2]/dt)$ is plotted against $\log[II]_0$. A good first-order relation with regard to II was obtained at concentrations below $\log[II]_0 = -0.7$ or about 0.2 mole/liter.

Effect of Illumination Intensity——No bromine was liberated in the dark. This indicates that light is necessary for the reaction. The rate of the reaction was measured at various intensities of irradiation keeping other conditions constant and results are shown in Fig. 5. The rate of the reaction was strongly influenced by the intensity of illumination.

Mechanism of the First Stage——The rate of the first stage of this reaction proved to be zero-order with regard to I, and first-order with regard to II and to be proportional to the intensity of irradiation. The following equation (1) was established from the above data.

$$\frac{d[Br_2]}{dt} = K \cdot Ir \cdot [II] \tag{1}$$

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6) Y. Ueno, S. Takemura, Y. Ando, and H. Terauchi, *Chem. Pharm. Bull.* (Tokyo), **15**, 1193 (1967).

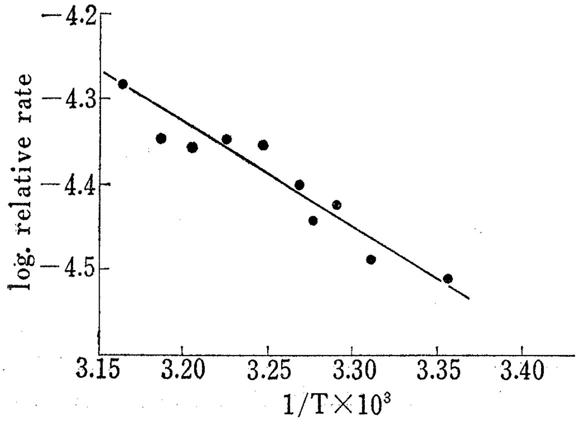

Fig. 2. Arrhenius Plot of the First Stage of the Reaction

reaction conditions
$[I]_0$: 0.05 mole/l CH_2Cl_2
$[II]_0$: 0.2 mole/l CH_2Cl_2
constant illumination

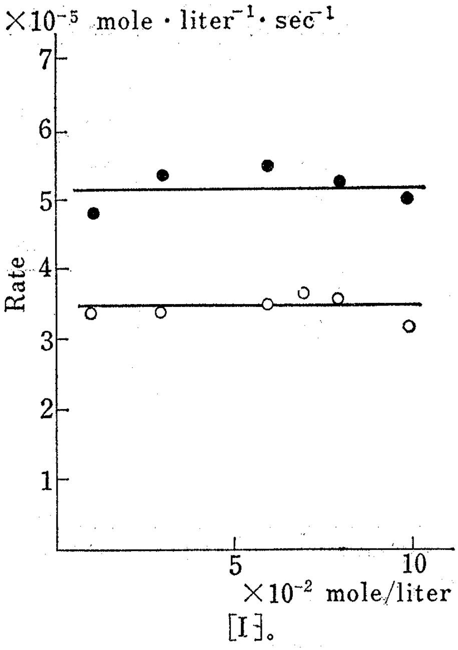

Fig. 3. Influence of [I] on the Rate of the First Stage of the Reaction

reaction conditions
$[II]_0$: 0.1 mole/l CH_2Cl_2
constant illumination
temperature: ● at 40°, ○ at 27°

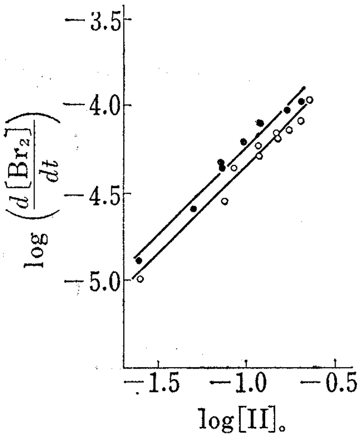

Fig. 4. Influence of [II] on the Rate of the First Stage of the Reaction

reaction conditions
$[I]_0$: 0.05 mole/liter CH_2Cl_2
$[II]_0$: 0.025—0.225 mole/liter CH_2Cl_2
constant illumination
temperature: ● at 40°, ○ at 27°

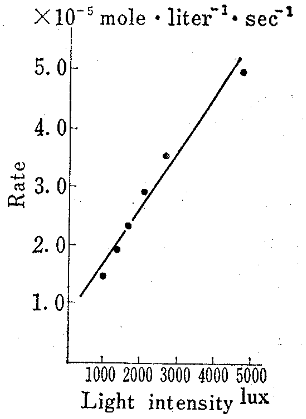

Fig. 5. Effect of Light Intensity on the Rate of the First Stage of the Reaction

reaction conditions
$[I]_0$: 0.05 mole/liter CH_2Cl_2
$[II]_0$: 0.1 mole/liter CH_2Cl_2
temperature: 31°

Thus, the reasonable mechanism of the first stage to explain those data may be as follows;

In the reaction of Eq. (2), I is excited by visible light. The excited I (I*) acts as a sensitizer in Eq. (3), and is reversibly deactivated as shown in Eq. (2). Equation (3) seems to be the ratedetermining step. From Eq. (4), benzenesulfonylnitrene must be produced besides the liberation of bromine. But the nitrene is obviously too labile to exist so long period in high concentration. The formation of some semistable complex between nitrene and something has presumed.³⁾ This intermediate is then considered in this paper to be a ylid-like complex (III) which may rather be formed directly than through nitrene, because

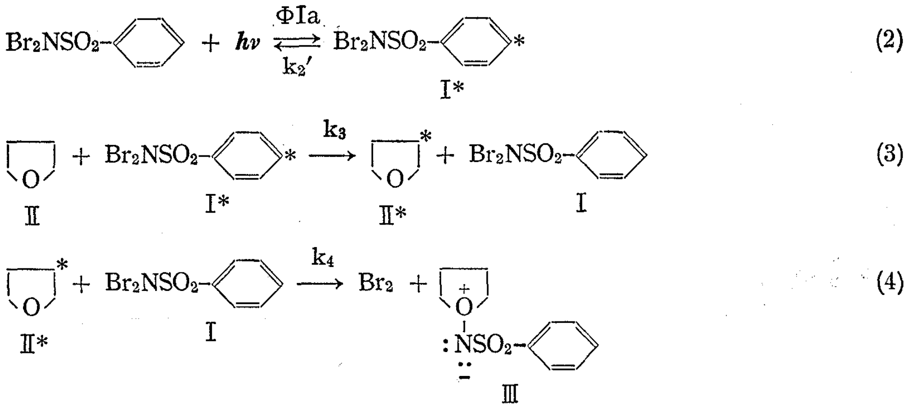

Chart 1

no nitrene derivative was found in the products when the reaction was run in the presence of benzene or cyclohexane. The analogous oxonium ion intermediate has been proposed in the reaction of ether with N_3CN by Marsh.[7]

Thus, the overall rate can be expressed as

$$\frac{d[\mathrm{Br_2}]}{dt} = \mathrm{k_4}\cdot[\mathrm{II}^*]\cdot[\mathrm{I}] \qquad (5)$$

If the usual steady state treatments are applied for [II*] assuming that $k_4 \gg k_3$, the equations used in the calculation may be as follows:

$$\frac{d[\mathrm{II}^*]}{dt} = \mathrm{k_3}[\mathrm{II}]\cdot[\mathrm{I}^*] - \mathrm{k_4}[\mathrm{II}^*]\cdot[\mathrm{I}] = 0 \qquad (6)$$

Assuming that step (2) is in partial equilibrium when $\Phi\mathrm{Ia} \gg \mathrm{k_3} \ll \mathrm{k_2}'$ we obtain Eq. (7).

$$\frac{d[\mathrm{I}^*]}{dt} = \Phi\mathrm{Ia} - \mathrm{k_2}'\cdot[\mathrm{I}^*] = 0 \qquad (7)$$

From Eqs. (5), (6), and (7), we can derive Eq. (8) for the rate.

$$\frac{d[\mathrm{Br_2}]}{dt} = \frac{\mathrm{k_3}\cdot\Phi\mathrm{Ia}}{\mathrm{k_2}'}[\mathrm{II}] \qquad (8)$$

This agrees fairly well with Eq. (1) established from the experimental data.

(2) Second Stage

Effect of the Concentration of Reactants——The effects of concentration of reactants (I and II) on the rate of consumption of bromine were studied at constant temperature. The plot of the decrease in the amount of bromine against time gave S-shaped curves, as shown in Fig. 6 and 7. Fig. 6 shows that this step was not dependent on [II]. Fig. 7 shows that [I] or $[\mathrm{Br_2}]$ has some influence on the reaction rate.

No stimulation was observed when a terminated reaction mixture of another run or a solution of HBr was added to the said reaction system at any moment of the second stage. It means that the accelerated intermediary rate is not catalyzed by the final product. Therefore the acceleration may be due to the rapid increase in concentration of some active intermediate. Thus, the S-shaped curve suggests that the reaction involves a nonstationary chain process.[8]

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7) F.D. Marsh, in "Nitrene," ed. W. Lwowski, John Wiley and sons, Inc., New York, 1970, p. 343.

8) Tutomu Kagiya, "Kinetics and Mechanism of Chemical Reaction (Part I)," Kagakudojin, Kyoto, 1970, p. 230.

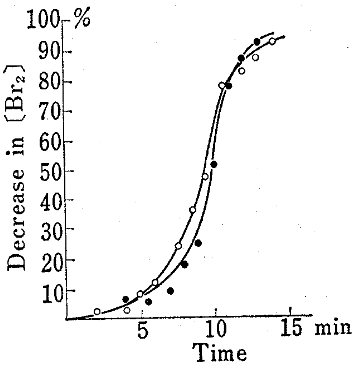

Fig. 6. Influence of II to the Rate of the Second Stage of the Reaction

reaction conditions
$[I]_0$: 0.05 mole/l CH_2Cl_2
250 lux and 18°
$[II]_0$: —●— 0.1 mole/l
—○— 0.5 mole/l

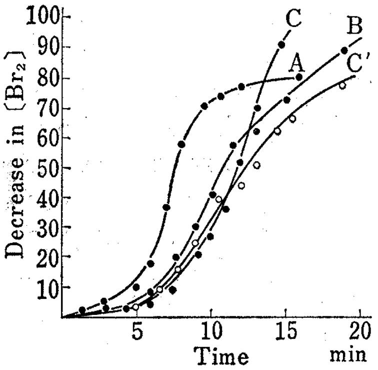

Fig. 7. Influence of $[Br_2]$ on the Rate of the Second Stage of the Reaction

reaction conditions
$[II]_0$: 0.2 mole/l CH_2Cl_2
250 lux and 18°
A: 0.1 mole/l $[Br_2]_0$
B: 0.05 mole/l $[Br_2]_0$
C: 0.03 mole/l $[Br_2]_0$
C′: 0.03mole/l $[Br_2]_0$+0.02 mole/l $[VIII]_0$

In the latter period of bromine-consumption, the rate decreases markedly. This decrease was greater at high $[I]_0$ (Fig. 7). In this period, the reaction seemed to be inhibited by its own product, benzenesulfonamide (VIII). Addition of VIII to a reaction system similar to that in Fig. 7-C decreased the rate of bromine-consumption in the latter period (Fig. 7-C′).

Mechanism of the Second Stage——These data may be explained by the reactions for the second stage shown below.

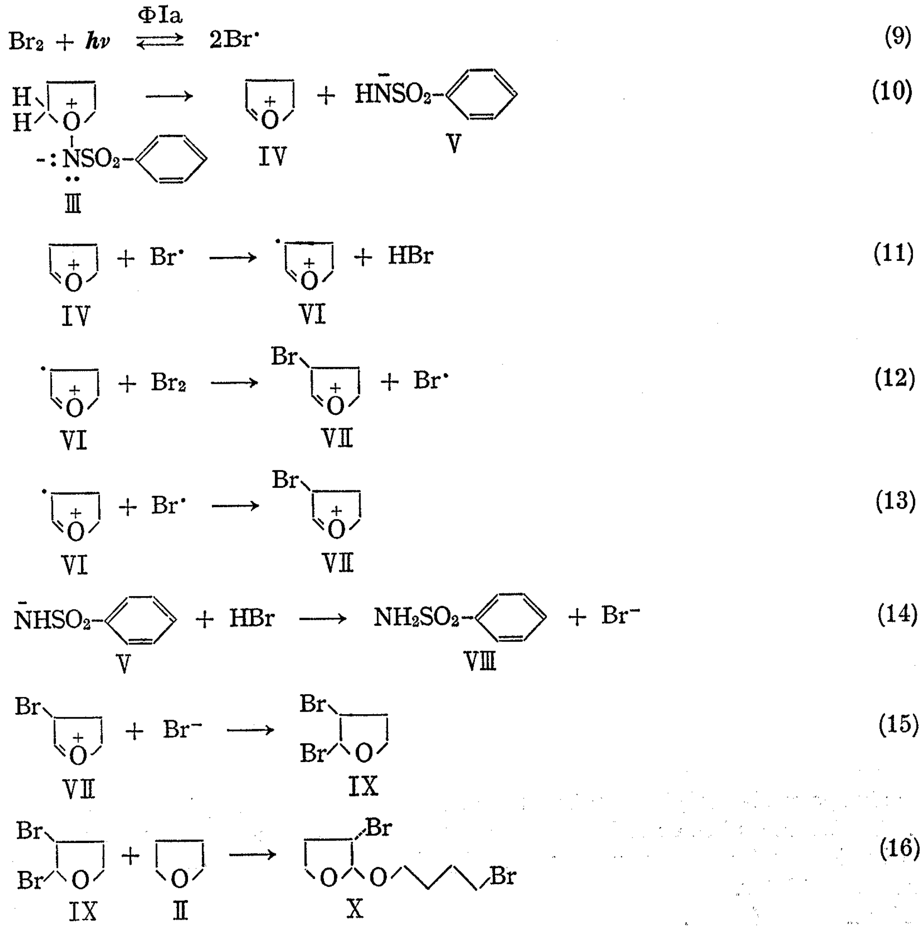

Chart 2

Second stage may be initiated by a photolysis of bromine. Elimination of the α-hydrogen and the benzenesulfonimino group from III may result an ion pair of the oxnium ion (IV) and V.9) The β-carbon of IV may combines with a bromine radical. The acceleration in the intermediary period would be explained by rapid increase of the active spesis, Br· and VI, with a chain process as shown with Eq. (11) and (12). The chain mechanism seems the most reasonable explanation of experimental data on the second stage. Nucleophilic bromination of the α-carbon of VII may yield 2,3-dibromotetrahydrofuran (IX).

On the other hand, no evidence was found that dihydrofuran was formed during any stage of the reaction, and IX had no influence on the reaction.

The reaction of IX with II may yield the final product X. Brief description of the reaction of the chloro-analogue have been given by Reppe10) and Lorette.11)

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9) *a*) A similar change of N-p-tolylsulfonylsulfilimine has been proposed by Tsujihara, *et al.* K. Tsujihara, T. Aida, N. Furukawa, and S. Oae, *Tetrahedron Letters*, **1970**, 3415; *b*) The presumption that is an intermediate of this reaction was also supported by the formation of γ-butyrolactone in the presence of water, as reported later.

10) W. Reppe, *Ann.*, **596**, 1 (1955).

11) N.B. Lorette, *J. Org. Chem.*, 23, 1590 (1958).