BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (12), 3426—3429 (1978)

The Reaction of Hydrogen Chloride with Nitrogen Oxide in Shock Waves

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(Received March 1, 1978)

The reaction of hydrogen chloride with nitrogen oxide in the temperature range 2670—3850 K and in the pressure range 2.5—3.5 atm has been studied behind reflected shock waves by monitoring the IR emission of HCl. When nitrogen oxide was added to the HCl–Ar system, the rate of HCl dissociation was found to be accelerated. For the early stage of reaction, the rate equation obtained was $-\mathrm{d}[\mathrm{HCl}]/\mathrm{d}t = 10^{11.7} \exp(-33\ \mathrm{kcal}/RT)[\mathrm{HCl}]^{1.3}[\mathrm{NO}]^{0.5}$ mol cm^{-3} s^{-1}. As the initiation step, Reaction 1 was found to be more important than Reaction 2 under these experimental conditions:

$$\mathrm{HCl} + \mathrm{NO} \longrightarrow \mathrm{HNO} + \mathrm{Cl}, \qquad (1)$$

$$\mathrm{HCl} + \mathrm{Ar} \longrightarrow \mathrm{H} + \mathrm{Cl} + \mathrm{Ar}. \qquad (2)$$

The rate constant of Reaction 1 was determined to be $k_1 = 10^{13.2} \exp(-50.2\ \mathrm{kcal}/RT)$ cm^3 mol^{-1} s^{-1}.

The reactions of NO with H_2 or NH_3 have been studied by several investigators.[1–5] Asaba and coworkers[1,2] found the initiation step to be the abstraction of a hydrogen atom by nitrogen oxide, and determined its rate constant. This is the only datum available for the abstraction reaction by nitrogen oxide at high temperatures. In this paper, in order to clarify the role of nitrogen oxide in the decomposition of hydrogen containing compounds, we studied the reaction of hydrogen chloride with nitrogen oxide in shock waves by monitoring the IR emission of HCl.

Experimental

The shock tube was 5 cm in internal diameter, as described previously.[6] All experiments were performed behind reflected shock waves. The IR emission from the fundamental vibration-rotation bands of HCl at 3.45 μm was detected by an AuGe detector through a CaF_2 window which was placed at a position 2 cm upstream from the end plate. The appropriate wavelength was selected by a grating monochromator. The output signal was amplified and recorded on an oscilloscope. The mole fractions of the samples were as follows: 4% HCl–96% Ar, 8% HCl–92% Ar, 4% HCl–4% NO–92% Ar, 4% HCl–8% NO–88% Ar, 8% HCl–4% NO–88% Ar, and 8% HCl–8% NO–84% Ar. The post-shock pressure (P_5) and temperature (T_5) were in the ranges 2.5—3.5 atm and 2670—3850 K, respectively.

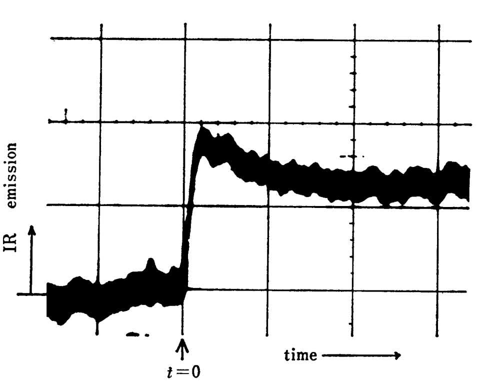

Fig. 1. A typical oscillogram of the IR emission at 3.45 μm. Run No. 231; conditions are summarized in Table 2. Sweep time=50 μs/division.

Results and Discussion

A typical oscillogram is shown in Fig. 1 (Run No. 231). This figure shows the IR emission at 3.45 μm, whose intensity corresponds to the concentration of HCl. The slow rise of the IR emission is due to the relatively long time constant (about 10 μs) of the AuGe detector. The rate of HCl dissociation ($-\mathrm{d}[\mathrm{HCl}]/\mathrm{d}t$) was obtained from the initial gradient of the IR emission intensity. The Arrhenius plots of $-\mathrm{d}[\mathrm{HCl}]/\mathrm{d}t$ obtained for four different mixtures are shown in Fig. 2. It is found that the rate of HCl dissociation was influenced by the initial concentrations of HCl and NO. The reaction orders with respect to the initial concentrations of HCl and NO were determined to be about 1.3 and 0.5, respectively. Thus,

$$-\mathrm{d}[\mathrm{HCl}]/\mathrm{d}t = k_{\mathrm{overall}}[\mathrm{HCl}]^{1.3}[\mathrm{NO}]^{0.5}.$$

The Arrhenius plot of k_{overall} thus obtained is shown in Fig. 3. The best fit line gives the overall rate constant as

$$k_{\mathrm{overall}} = 10^{11.7} \exp(-33\ \mathrm{kcal}/RT)\ \mathrm{cm}^{2.4}\ \mathrm{mol}^{-0.8}\ \mathrm{s}^{-1}.$$

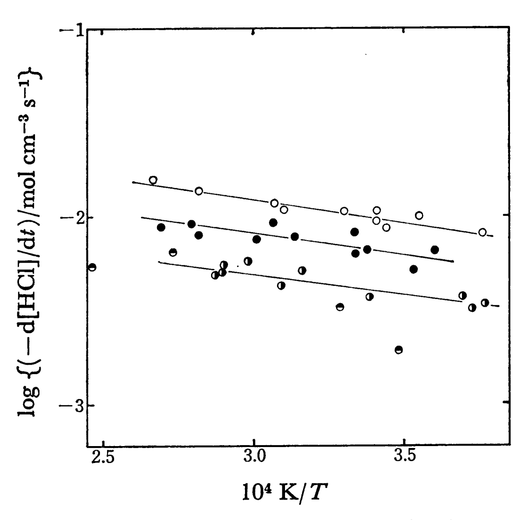

Fig. 2. Arrhenius plots of $-\mathrm{d}[\mathrm{HCl}]/\mathrm{d}t$ obtained for different mixtures. ○: 8% HCl–8% NO–84% Ar, ●: 8% HCl–4% NO–88% Ar, ◑: 4% HCl–8% NO–88% Ar, ◒: 4% HCl–4% NO–92% Ar.

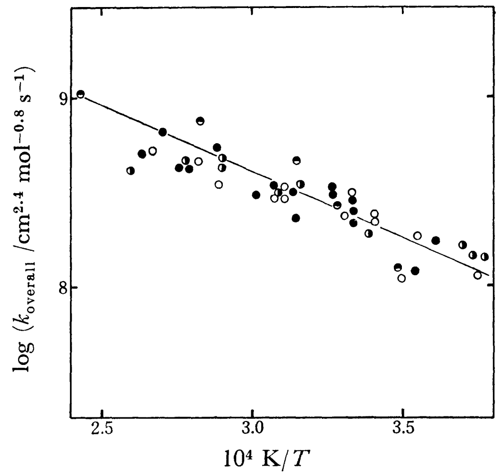

Fig. 3. Arrhenius plot of $k_{overall}$.] Symbols are the same as in Fig. 2.

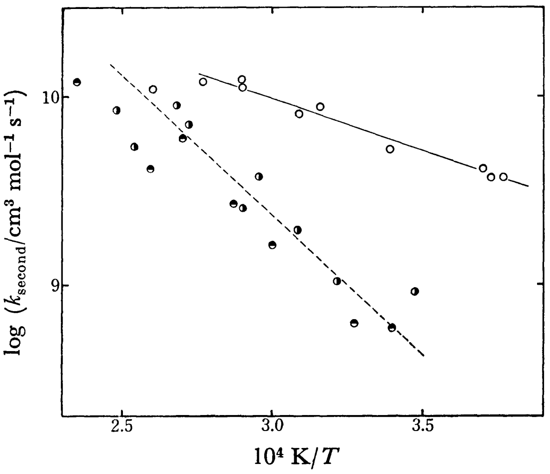

Fig. 4. Arrhenius plots of k_{second} for the mixtures with NO (○) and without NO (◑, ◓). ○: 4% HCl–8% NO–88% Ar, ◑: 4% HCl–96% Ar, ◓: 8% HCl–92% Ar, ---: Jacobs *et al.*[7]

In order to check the experimental method used in this work, HCl–Ar mixtures were also shock-heated and the rates of HCl dissociation were measured similarly. In Fig. 4, the second order rate constants, $k_{second}=(-d[HCl]/dt)/[HCl][Ar]$, are plotted in the Arrhenius form for mixtures with and without NO. In this figure, the data obtained by Jacobs *et al.*[7] are also shown by a broken line. In spite of different experimental conditions and methods of the data reduction in the two works, our rate data for the HCl dissociation without NO are in good agreement with those of Jacobs. It was also found, as seen in Fig. 4, that the rate of HCl dissociation was accelerated by the addition of NO, and this effect was more remarkable at lower temperatures.

To clarify the dissociation kinetics of hydrogen chloride in the system involving nitrogen oxide, 26 elementary reactions (Mechanism I) were selected and tabulated in Table 1. Values of the rate constants for Reactions 2—26 were cited from the references. The numerical integrations of simultaneous rate equations for 15 species listed in Table 1 were performed on an electronic computer to obtain the time histories of the concentrations of the reactants and products. There are no data for the rate constant of Reaction 1. Thus in the calculations the value of k_1 was varied in the range 10^9—2×10^{10} cm^3 mol^{-1} s^{-1}, and the value of k_1 was determined as the value at which the calculated history of HCl agreed best with that obtained from experiment. The fit of the calculations to the experiment is shown

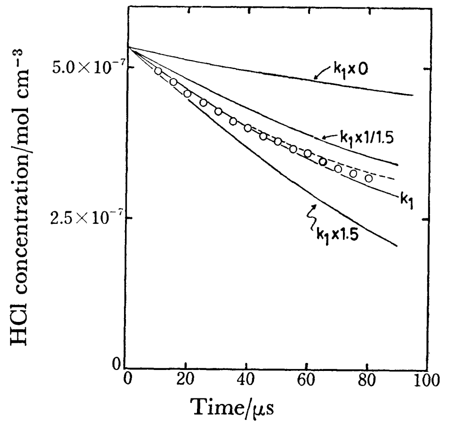

Fig. 5. Time histories of HCl calculated with various k_1 values for the conditions of Run No. 322. ○: Observed history, —: calculated histories for Mechanism I, ---: calculated history for Mechanism II. The best fit value of k_1 is 3.00×10^9 cm^3 mol^{-1} s^{-1}. The value of k_1 is varied from 0 to 1.5 times the best value.

Table 1. ELEMENTARY REACTIONS AND ASSIGNED RATE CONSTANTS, $k=AT^B\exp(-E/RT)$

	Reaction	log A[a)]	B	E (kcal/mol)	Ref.
1	$HCl+NO \to HNO+Cl$	13.2	0.0	50.2	This work
2	$HCl+Ar \to H+Cl+Ar$	12.82	0.0	70.0	7
3	$HNO+Ar \to H+NO+Ar$	16.5	0.0	49.0	11
4	$HCl+H \to H_2+Cl$	13.36	0.0	3.5	12, 14
5	$H_2+Cl \to HCl+H$	13.68	0.0	5.26	13
6	$HCl+Cl \to H+Cl_2$	13.85	0.0	48.0	14, 15
7	$Cl_2+H \to HCl+Cl$	14.2	0.0	1.96	15
8	$Cl_2+Ar \to 2Cl+Ar$	13.94	0.0	44.8	16
9	$H_2+Ar \to 2H+Ar$	14.34	0.0	96.0	11
10	$H+NO \to OH+N$	13.7	0.0	48.7	2
11	$N+NO \to N_2+O$	13.2	0.0	0.0	11
12	$O+HCl \to OH+Cl$	12.76	0.0	5.9	17
13	$OH+HCl \to H_2O+Cl$	12.98	0.0	1.0	18
14	$H_2O+H \to H_2+OH$	13.97	0.0	20.6	11
15	$OH+H \to H_2+O$	9.5	1.0	7.0	11
16	$2H+Ar \to H_2+Ar$	17.81	−1.0	0.0	11
17	$2Cl+Ar \to Cl_2+Ar$	13.3	0.0	−11.3	16
18	$H_2+O \to OH+H$	10.25	1.0	9.96	11
19	$H_2+OH \to H_2O+H$	13.35	0.0	5.2	11
20	$2O+Ar \to O_2+Ar$	15.78	−0.5	0.0	11
21	$O_2+Ar \to 2O+Ar$	14.41	0.0	108.0	11
22	$H+O_2 \to OH+O$	14.34	0.0	0.0	11
23	$OH+O \to H+O_2$	13.1	0.0	0.0	11
24	$NO+O \to N+O_2$	9.18	1.0	38.5	11
25	$O+Cl_2 \to ClO+Cl$	12.8	0.0	3.6	19
26	$O+ClO \to O_2+Cl$	13.5	0.0	0.0	20

a) Units: mol cm^{-3} for concentration, s for time.

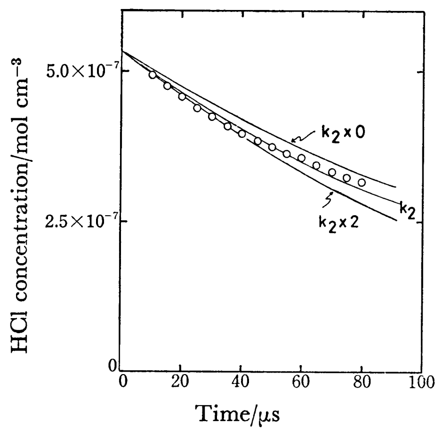

Fig. 6. Time histories of HCl calculated with various k_2 values for the conditions of Run No. 322. ○: Observed history, —: calculated histories for Mechanism I. The best fit value of k_2 is $k_2 = 10^{12.82}$ exp (−70 kcal/RT)[7] cm^3 mol^{-1} s^{-1} (middle curve). The value of k_2 is varied from 0 to 2 times the best-fit value.

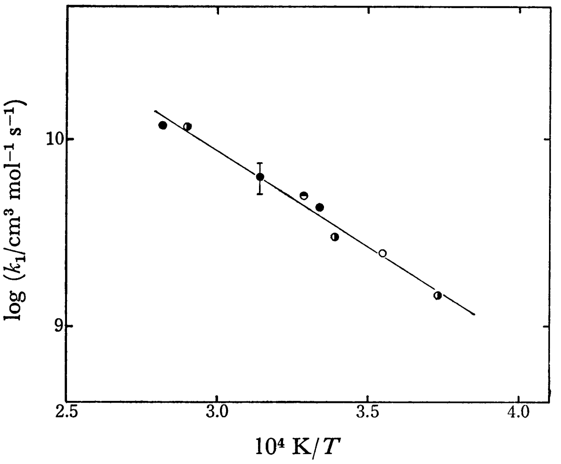

Fig. 7. Arrhenius plot of k_1. The error bar indicates the ±25% maximum uncertainty. Symbols are the same as in Fig. 2.

in Fig. 5 for Run No. 322 as an example. For checking the sensitivity, the value of k_1 was varied from 0 to 1.5 times the best value, and the histories of HCl were recalculated by using these values. The histories thus obtained are also shown in Fig. 5. From Fig. 5, it appears that the rate of HCl dissociation is strongly influenced by the value of k_1. The sensitivity of k_2 to the overall rate of HCl dissociation was also checked.

The value of k_2 was varied from 0 to 2 times that listed in Table 1. Figure 6, which shows the results of the calculations for Run No. 322, reveals that the variation in k_2 has very little effect on the overall rate. Therefore, Reaction 1 is found to be predominant as the initiation step. The experimental conditions used for the estimation of k_1 and the values of k_1 determined at various temperatures are listed in Table 2. The Arrhenius plot of k_1 is shown in Fig. 7. The best fit line of the plot gives the rate expression as

$$k_1 = 10^{13.2} \exp(-50.2\ \mathrm{kcal}/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

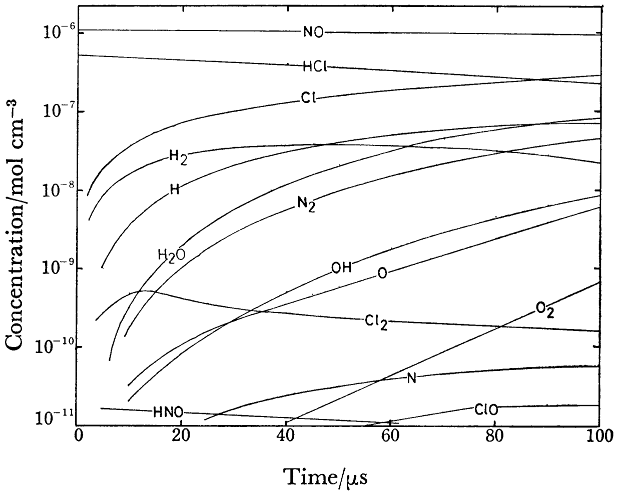

Fig. 8. Time dependent concentration changes of chemical species calculated with Mechanism I for the conditions of Run No. 322.

Figure 8 shows the time variation of the concentration of each chemical species for Run No. 322. The figure implies that Mechanism I can be reduced to only the first eight elementary reactions (1—8) (Mechanism II), since in the initial stage of reaction nitrogen oxide does not decrease largely and thus H_2O, OH, N_2, O, N, *etc.* are neglected. The calculated history of HCl for Mechanism II is shown by the broken line in Fig. 5.

Since the experimentally determined reaction orders were the average values in the initial stage (from 0 to about 30 μs), the reaction orders for HCl and NO, which were averaged between 0 and 30 μs, were calculated by using Mechanism I. The values calculated for HCl and NO were 1.06 and 0.62, respectively. Thus, the calculated reaction orders are comparable to the values determined experimentally. The rate of HCl

Table 2. Experimental conditions and determined rate constants

Run No.	Temp (K)	HCl (mol cm^{-3})	NO (mol cm^{-3})	Ar (mol cm^{-3})	−d[HCl]/dt (mol cm^{-3} s^{-1})	k_1 (cm^3 mol^{-1} s^{-1})
231	3185	9.295×10^{-7}	4.647×10^{-7}	1.023×10^{-5}	7.62×10^{-3}	6.23×10^9
232	2996	10.18	5.089	1.119	6.36	4.30
235	3544	8.062	4.031	0.887	8.02	11.6
261	3044	5.100	5.100	1.173	3.29	4.95
281	2819	11.94	11.94	1.253	10.6	2.46
321	2678	5.859	11.72	1.289	3.26	1.48
322	2949	5.345	10.69	1.176	3.75	3.00
331	3447	4.301	8.602	0.946	5.29	11.5

dissociation in Mechanism II is expressed as

$$-\mathrm{d[HCl]}/\mathrm{d}t = \underbrace{k_1[\mathrm{HCl}][\mathrm{NO}]}_{\text{term A}} + \underbrace{k_2[\mathrm{HCl}][\mathrm{Ar}]}_{\text{term B}} + \underbrace{(k_4[\mathrm{H}][\mathrm{HCl}] - k_5[\mathrm{H_2}][\mathrm{Cl}])}_{\text{term C}} + \underbrace{(k_6[\mathrm{Cl}][\mathrm{HCl}] - k_7[\mathrm{Cl_2}][\mathrm{H}])}_{\text{term D}}.$$

The contributions of terms A, B, C, and D to the rate of HCl dissociation are shown in Fig. 9 as a function of time for the conditions of Run No. 322. From this figure, it is found that terms A and C are important for the HCl consumption.

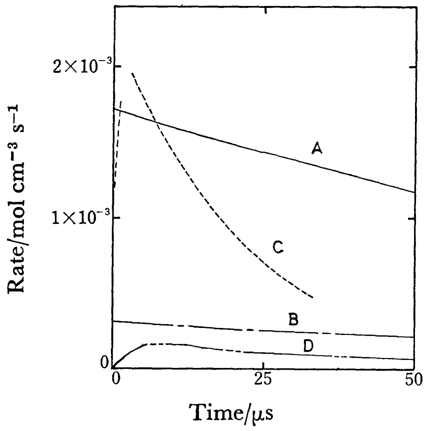

Fig. 9. Time variations of rate terms which contribute to the HCl dissociation. Symbols A, B, C, and D are explained in the text.

As the initiation step, the following three reactions are possible:

$$\mathrm{HCl + NO \longrightarrow HNO + Cl}, \quad \Delta H^\circ_{298} = 53.2\ \mathrm{kcal\ mol^{-1}}, \qquad (1)$$

$$\mathrm{HCl + NO \longrightarrow H + ClNO}, \quad \Delta H^\circ_{298} = 65.0\ \mathrm{kcal\ mol^{-1}}, \qquad (1')$$

$$\mathrm{HCl + Ar \longrightarrow H + Cl + Ar}, \quad \Delta H^\circ_{298} = 103.1\ \mathrm{kcal\ mol^{-1}}, \qquad (2)$$

where the standard enthalpy changes (ΔH°_{298}) were calculated from JANAF Thermochemical Tables.[21] Reactions 1 and 1′ are not distinguishable because the decomposition rates of HNO and ClNO are very fast. However, because Reaction 1′ is more endothermic by 12 kcal mol^{-1} than Reaction 1, it seems to be reasonable to neglect Reaction 1′ as the initiation step. As shown in Fig. 6, even if Reaction 2 was ruled out, the rate of HCl dissociation did not change very much. Therefore, Reaction 1 was confirmed to be a more important initiation step than Reaction 2.

The activation energy of Reaction 1 was calculated by the bond-energy-bond-order (BEBO) method, which was developed by Johnston and Parr,[22,23] as 52.7 kcal mol^{-1}. The activation energy which was obtained in this work, 50.2 kcal mol^{-1}, is very close to this calculated value. It is interesting to compare the rate constant with that for a similar reaction

$$\mathrm{H_2 + NO \longrightarrow HNO + H}. \qquad (27)$$

The rate constant of Reaction 27 was obtained as[2]

$$k_{27} = 10^{13.5} \exp(-55.2\ \mathrm{kcal}/RT)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

This activation energy is nearly equal to the standard enthalpy change (54.3 kcal mol^{-1}) of the reaction. The value of the A factor for k_{27} is larger than for k_1 by a factor of about 2. This difference is greater than the experimental error of ±25% maximum uncertainty in the determination of k_1. Since the ratio of the collision number for the $\mathrm{H_2}$–NO system to that for the HCl–NO system was calculated as

$$Z_{\mathrm{H_2-NO}}/Z_{\mathrm{HCl-NO}} = 2.7,$$

the difference of the A factor may be due to the difference of collision numbers for Reactions 1 and 27.

The authors wish to thank Professor T. Asaba and Dr. N. Fujii of the University of Tokyo for providing us with the computer program.

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