THE REACTION BETWEEN HYDROGEN CHLORIDE AND NITROGEN PEROXIDE*

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The reaction between hydrogen chloride and nitrogen peroxide has been studied in the temperature range 25-55°C. The reaction is heterogeneous, and dinitrogen tetroxide is the reactive species. In a glass reaction vessel the rate is proportional to $P_{\rm N_2O_4}^{1.02}$ and is independent of $P_{\rm HCl}$. The value of the velocity constant is given by

 $k = 10^{3.16} \exp(-12,883/RT) \sec^{-1}$.

The products of the reaction are NOCl, Cl_2 and H_2O . When the reaction vessel is coated with paraffin wax the reaction rate is reduced, and is proportional to $P_{N_2O_4}^{0.65} P_{HCl}^{0.58}$. A mechanism is suggested to explain the results.

Harris and Siegel¹ showed that hydrogen chloride reacted with nitrogen peroxide in the dark at room temperature, and stated the stoichiometric equation to be $NO_2 + 2 \text{ HCl} \rightarrow \text{NOCl} + \text{H}_2\text{O} + \frac{1}{2}\text{Cl}_2$. The present paper describes a study of the kinetics and mechanism of this reaction in the temperature region 25-55°C. This work is the first of a series of investigations into the reactions of nitrogen peroxide with halogens and their derivatives.

EXPERIMENTAL

MATERIALS

Nitrogen peroxide and nitrogen were prepared as described earlier.²

Hydrogen chloride was prepared by the reaction of 75 % A.R. sulphuric acid and A.R. sodium chloride. After partial drying over silica gel or calcium chloride it was condensed at the temperature of liquid air, and then distilled into a reservoir through a trap at -80° C.

Chlorine was supplied in cylinders by Messrs. I.C.I. Ltd., and purified by drying over phosphorus pentoxide, followed by distillation after condensing at the temperature of liquid air.

"High purity" hydrogen was supplied by the British Oxygen Co. Ltd., and was dried by passing through a trap cooled in liquid air.

Nitric oxide was prepared by the reaction between potassium nitrate and potassium iodide in acid solution according to the method of Johnston and Giauque.³ It was purified by fractionation.

Nitrosyl chloride was prepared by the action of nitrogen peroxide on moist potassium chloride according to the method of Whittaker, Lundstrom and Merz.⁴ The gas was dried over phosphorus pentoxide and purified by fractionation. It was kept as the solid over liquid air in a darkened vessel.

The water used was distilled and degassed several times in vacuo.

APPARATUS

This was of the usual high-vacuum type constructed in Pyrex glass. Four different reaction vessels were used as follows: vessel 1, a spherical vessel, capacity 320 ml; surface/volume ratio 0.80. Vessel 2, a spherical vessel packed with short lengths of

* Throughout this paper the term nitrogen peroxide is used for the equilibrium mixture $2 \text{ NO}_2 \rightleftharpoons N_2O_4$. The names nitrogen dioxide (NO₂), and dinitrogen tetroxide (N₂O₄) refer to the monomer and dimer respectively.

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4-mm Pyrex tubing, capacity 346 ml; surface/volume ratio 7.57. Vessel 3, a spherical vessel coated on the inner surface with a film of paraffin wax, capacity 320 ml; surface/volume ratio 0.75. Vessel 4, a spherical vessel coated with paraffin wax and packed with small pieces of paraffin wax, approximately $35 \times 4 \times 4$ mm, capacity 207 ml; surface/volume ratio 5.4. The reaction vessels were painted black to avoid photolysis of the NOCI formed in the reaction, and immersed in an electrically-heated oil-filled thermostat. Rates of reaction were measured manometrically using a glass-spiral gauge 5 as a direct-reading instrument. For the admission of the larger pressures of the reactants the gauge was used as a null-point instrument in conjunction with an external mercury manometer. Pressure changes could be measured to 0.03 mm. All taps and joints coming into contact with the reaction products were lubricated with silicone high-vacuum grease. This grease was attacked slowly by the reaction products, but as the tap to the reaction vessel was a capillary one, very little grease was in contact with the products during our experiments, and trials showed that the attack on the grease could be neglected during the course of an experimental run.

In order to obtain reproducible results it was necessary to evacuate the reaction vessel for about 5 h at 100°C. Under these conditions smooth curves were obtained from which the initial rates could be estimated to within $\pm 2 \%$.

The reaction products were separated by gas-liquid partition chromatography at room temperature, using a 12-ft. column of Celite 545 and dimethyl phthalate (50 % w/w), and hydrogen as carrier gas. The apparatus was similar in design to that described by Callear and Cvetanovic.⁶ Individual components of the reaction products were condensed separately in traps cooled in liquid air, and estimated by measuring the pressure after allowing them to expand into a vessel of known volume. One limb of the manometer used was partially filled with air to prevent contamination of the mercury by the products.

RESULTS

ANALYSIS OF PRODUCTS.

The products of the reaction were completely absorbed by sodium hydroxide, and they showed no appreciable vapour pressure at the temperature of liquid air. This eliminates nitrogen, hydrogen, oxygen, nitric oxide, and nitrous oxide as possible products.

The majority of analytical experiments were carried out using excess HCl in order to avoid any residual nitrogen peroxide, since it was not found possible to obtain a satisfactory separation of nitrogen peroxide from the reaction products, using the chromatographic column described above. With excess HCl the products were separated into three components by the chromatographic method. Component 1 was identified spectroscopically as chlorine, and this was confirmed by comparing its retention volume in the column with that of a sample of chlorine. Component 2 was a white solid at the temperature of liquid air (and changed to a brick red in the presence of traces of water). It was completely gaseous at -80° C. The gas was completely absorbed in potassium hydroxide, and the resulting solution gave a positive test for chloride. The retention volume for this component was the same as that for a sample of HCl, and was thus identified as this substance. Component 3 was an orange yellow solid at the temperature of liquid air and melted to a blood-red liquid. Its retention volume agreed with that of a sample of NOCl. The melting point of the component was -57.5° C, the melting point of NOCl is given as -59.6° C.⁷ This temperature is nearly 50° away from the melting point of any other possible reaction product or reactant, and thus component 3 was identified as NOCI. The other possible product of the reaction, water, was retained by the column but its presence in the products was shown by adding anhydrous copper sulphate to the products of the reaction condensible at -80° C. The copper sulphate turned blue. Water was subsequently estimated by difference.

Two typical analyses of the reaction products are given in table 1, for reactions at 55°C in reaction vessels 1 and 2. The pressures given are those that would be exerted by the various components in the vessel at 55°C. The value for $P_{\rm H_2O}$ was calculated on the assumption that all the hydrogen in the hydrogen chloride which reacts is oxidized to water.

In the analysis of reaction products from vessel 1, 1.87 mm of the final pressure of 35.4 mm are unaccounted for. The atom balance shows that the loss corresponds closely to NOCl. For vessel 2, 1.15 mm of the final pressure of 35.05 mm are unaccounted for, and here the loss corresponds to Cl₂.

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TABLE 1.—ANALYSIS OF PRODUCTS (pressure in mm Hg)

TE	мр. 55°С									
	P _{initial} nitrogen peroxide	P _{initial} HCl	P _{final}	P _{NOC1}	P_{Cl_2}	P _{HCl} F	H ₂ O ^(calc.)	una N	ccounted O	l for Cl
vessel 1	10	30	35.4	8.43	5.0	10.2	9.9	1.8 *	1.9 *	1.37
vessel 2	10	30	35.05	9.8	4.5	9.2	10.4	0·4 *	0.0 *	2.0

* In calculating these values allowance has been made for the small amount of N2O4 present in the nitrogen peroxide (~ 1 %).

In view of the great reactivity of these substances, and their attack on the tap greases, the analysis is in good agreement with Harris and Siegel, viz.,

$$NO_2 + 2 HCl \rightarrow NOCl + H_2O + \frac{1}{2}Cl_2,$$
 (a)

$$\frac{1}{2}N_2O_4 + 2 \operatorname{HCl} \rightarrow \operatorname{NOCl} + \operatorname{H}_2O + \frac{1}{2}\operatorname{Cl}_2. \tag{b}$$

KINETIC MEASUREMENTS

In the temperature region in which these experiments were performed (25-55°C) nitrogen peroxide exists as an equilibrium mixture of the monomer NO2 and the dimer N_2O_4 . At the pressures of nitrogen peroxide used (up to 25 mm Hg), the pressure of the N₂O₄ present (calculated according to the data of Giauque and Kemp ⁸) was always less than 5 % of the total pressure. In expressing the pressures of NO_2 , allowance has been made for this small amount of dimer and thus P_{NO_2} is the true NO₂ pressure, and $P_{N_2O_4}$ refers to the true N_2O_4 pressure. If NO₂ is the reactive species, the stoichiometric equation is (a) above, and $-dP/dt = -\frac{1}{2}dP_{NO_2}/dt$, where P is the total pressure of the reaction mixture. (Under the conditions of the experiment $P_{N_2O_4}$ is small as stated above and the re-establishment of the equilibrium by the reaction $N_2O_4 \rightarrow 2 NO_2$ will have a negligible effect on the overall pressure.) If N_2O_4 is the reactive species, the stoichiometric equation is (b) above. This equation as it is written shows no decrease in pressure. The observed decrease results from the reaction $2 \text{ NO}_2 \rightarrow \text{N}_2\text{O}_4$ which takes place rapidly to mainta'n the equilibrium. Under these conditions

$$-\mathrm{d}P/\mathrm{d}t = -\mathrm{d}P_{\mathrm{N}_2\mathrm{O}_4}/\mathrm{d}t.$$

ORDER OF REACTION .- Since either NO2 or N2O4 could be the reactive species the order of reaction has been calculated for both. Reaction vessel 1 was used throughout.

(a) Nitrogen dioxide.—Measurement of the initial rates of a series of runs in which the initial pressure of HCl was constant, and in which the initial pressure of NO₂ varied, showed that the rate was proportional to $P_{NO_2}^{2.04}$. A plot of log P_{NO_2} against log (initial rate) is shown in fig. 1 for a series of experiments at 55°C.

(b) Dinitrogen tetroxide.—The pressure of N_2O_4 is related to that of NO_2 by the expression $P_{NO_2}^2 = K_p P_{N_2O_4}$ (where K_p is the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$) thus

$$d \log P_{\rm NO_2} = \frac{1}{2} d \log P_{\rm N_2O_4}$$

The rate will therefore vary as $P_{N_2O_4}^{1.02}$.

(c) Hydrogen chloride.—Variation of the initial concentration of HCl for a constant initial concentration of nitrogen peroxide had no effect on the initial rate of the reaction. The order in HCl is therefore zero (see fig. 1). Thus if NO_2 is the reactive species,

$$- \mathrm{d} P_{\mathrm{NO}_2}/\mathrm{d}t = k_{\mathrm{NO}_2} P_{\mathrm{NO}_2}^{2.04} P_{\mathrm{HCl}}^{0.0}$$
;

if N_2O_4 is the reactive species,

$$- dP_{N_2O_4}/dt = k_{N_2O_4} P_{N_2O_4}^{1\cdot 02} P_{HCl}^{0\cdot 0}.$$

ACTIVATION ENERGY.—The reaction was studied in vessel 1 over the temperature region 25-55°C using constant initial pressures of nitrogen peroxide and HCl. Since the amount of NO_2 in the nitrogen peroxide varied with temperature the initial rates measured were corrected to a constant initial pressure of NO2, using the order in NO2 already established. Correction was also made for the change in concentration brought about by

or

the change in temperature. Fig. 2 shows a plot of the logarithm of the initial rate against $1/T^{\circ}K$ for a constant initial concentration of NO₂. From the slope of this line the



activation energy is calculated as -810 ± 500 cal mole⁻¹ assuming NO₂ to be the reactive species. If N₂O₄ is the reactive species this value will be increased by the heat of dissociation ⁹ of N₂O₄ ($\Delta H_{293}^{\circ} = 13,693$ cal) to give the value 12,883 cal mole⁻¹.

The velocity constants for the reaction are calculated as

$$k_{\text{NO}_2} = 10^{6\cdot78} \exp(810/RT) \text{ l. mole}^{-1} \text{ sec}^{-1},$$

$$k_{\text{N}_2\text{O}_4} = 10^{8\cdot16} \exp(-12,883/RT) \text{ sec}^{-1}.$$

At 55°C $k_{\text{NO}_2} = 21\cdot0$ l. mole⁻¹ sec⁻¹, and $k_{\text{N}_2\text{O}_4} = 0.398 \text{ sec}^{-1}.$
(NOTE.— $k_{\text{N}_2\text{O}_4} = \frac{1}{2} k_{\text{NO}_2} K_c.$)

EFFECT OF SURFACE.—(a) When vessel 1 was replaced by vessel 2, thus increasing the surface/volume ratio nine-fold, the initial rate of the reaction was increased by a factor of approximately 6 (see table 2). The increase in surface area in this vessel did not affect the order in HCl which remained at zero.

		TABL	.е 2.—Е	FFECT O	F SURFAC	CE ON INT	FIAL R	ATE	
темр.	55°C			P _{nitroger} peroxide	$g = 7.5 \mathrm{m}$	nm		P _{HCl}	= 50∙0 mm
				initial 1	rate (mm/r	nin)			
		vesse	11	1.2,		vessel 2		7·0.	
TEMP.	25°C			P _{nitrogen} peroxid	$r_e = 15 \mathrm{m}$	m		P _H	$_{Cl} = 50 \text{ mm}$
	vessel	1	5·0,	initial vesse	rate (mm/) 1 3 0	min) •65,	vessel	4	2.85.

(b) The experiments with vessel 2 showed the reaction was strongly surface dependent and therefore vessel 2 was replaced by the paraffin-wax-coated vessel 3, whose surface



was less polar. Most of the experiments in this vessel were made at 25° C, since the wax film was not mechanically stable at 55° C. At 25° C the initial rate of a particular mixture of nitrogen peroxide and HCl was found to be less than the rate in vessel 1 by a factor of 8 (see table 2). Moreover this vessel produced a change in the orders in NO₂ and HCl, as is shown by the plots of log (initial rate) against log P_{NO_2} and log P_{HCl} in fig. 3. In this vessel the order in NO₂ was 1.3 (N₂O₄ order, 0.65), and in HCl was 0.58.

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(c) About 9 % of the surface of vessel 3 was not coated with paraffin wax (this portion consisted of the capillary leads to the manometer and tap). In order to minimize the possible effects of this glass surface, vessel 3 was packed with pieces of paraffin wax (vessel 4). Under these conditions the rate was found to be four times greater than that in vessel 3 for the same reaction mixture. This shows that the paraffin wax surface was by no means inert, and that the reaction in this vessel could not be attributed to reaction on the residual glass surface. It also suggests that the amount of homogeneous reaction at these temperatures is very small.

EFFECT OF ADDITIVES.—The addition of the following substances at the pressures stated, to a mixture of 50 mm of HCl and 17.4 mm nitrogen peroxide at 55°C had no effect on the initial rate of the reaction :

nitrogen	up to 80 mm pressure,
nitric oxide	up to 40 mm pressure,
hydrogen	up to 20 mm pressure,
nitrosyl chloride	up to 30 mm pressure,
chlorine	up to 10 mm pressure.

Addition of nitrogen at a pressure of 200 mm caused a decrease in initial rate from 5.9 mm/min to 5.2 mm/min. The addition of water vapour to a mixture of 50 mm HCl and 7.5 mm nitrogen peroxide in vessel 2 caused a marked reduction in rate as shown in table 3.

TABLE 3.—EFFECT OF WATER VAPOUR (VESSEL 2)

temp. $55^{\circ}C$

	$P_{\text{nitrogen}} = 7.5 \text{ mm}$	$P_{\rm HCl} = 50.0 \rm mm$
$P_{\rm H_2O}(\rm mm)$		initial rate (mm/min)
0		7.0
7.5		5.5
10.0		4.36
15.1		2.1

NATURE OF REACTIVE SPECIES.—The kinetic experiments described do not clearly establish the reactive species in the reaction as NO₂ or N₂O₄. However, the negative activation energy and extremely low pre-exponential factor found on the assumption that NO₂ is the reactive species, suggest that this assumption is incorrect. This is supported by the work of Pollard and Holbrook ¹⁰ on the heterogeneous reaction between formic acid and NO₂, who find this reaction to have the second-order rate constant $k = 10^{6.73} \exp(-16,276/RT)$ l. mole⁻¹ sec⁻¹. As it is impossible to obtain pure NO₂ or pure N₂O₄ at the temperatures of these experiments, the reaction between HCl gas and solid N₂O₄ was examined at - 80 °C. At this temperature, nitrogen peroxide exists in the dimeric form only.

A measured amount of nitrogen peroxide was frozen into a small tube cooled in liquid air. This was followed by the freezing of a measured amount of HCl into the same tube. The liquid-air container was then replaced by one containing a solid carbon dioxide + acetone mixture, and the tube allowed to warm to -80° . At this temperature the N₂O₄ is a solid and the HCl a gas. After 10 min the HCl pressure fell from an initial value of 50 mm to 42 mm and after a further 20 min to 36 mm. At this time in addition to the original white N₂O₄, the tube contained a blue solid (typical of a mixture of solid N₂O₄ and water), and an oily orange liquid similar in appearance to that of the reaction products at this temperature. This experiment showed that there was undoubtedly a reaction between solid N₂O₄ and HCl gas, and a calculation from the pressure change showed that 75 % of the original HCl had reacted after 30 min. This evidence, together with that of the kinetic measurements, strongly suggests that N₂O₄ is the reactive species in this reaction.

DISCUSSION

The results of this work are best explained in terms of a mechanism in which the HCl is strongly adsorbed on the surface of the vessel, and the reaction takes place between this adsorbed HCl and N_2O_4 .

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If the amount of HCl on the surface increases by adsorption and decreases by reaction, a steady state will be reached at which the rate of increase will equal the rate of decrease. Let the fraction of the surface covered by hydrogen chloride at this point be σ . Then,

rate of adsorption of $HCl = k'[HCl](1 - \sigma)$,

rate of removal by reaction = $k''[N_2O_4]\sigma$.

Hence

$$\sigma = k'[\text{HCl}]/(k'[\text{HCl}] + k''[\text{N}_2\text{O}_4]).$$

The rate of reaction = $k''[\text{N}_2\text{O}_4]\sigma = \frac{k'k''[\text{HCl}][\text{N}_2\text{O}_4]}{k'[\text{HCl}] + k''[\text{N}_2\text{O}_4]}.$

Thus if $k' \gg k''$, the reaction rate $= k''[N_2O_4]$ in agreement with experiment. Under these circumstances the surface will be almost completely covered by HCl. The work of Cherkov and Goldanskii¹¹ has shown HCl to be strongly adsorbed on glass surfaces in accordance with this theory.

If $k' \sim k''$, the rate would approximate to the form, rate $= k[\text{HCl}]^x[N_2O_4]^y$, where x and y are less than one. This is the relationship found on a paraffin-wax surface, where the adsorption of HCl would be expected to be less than on glass. The inhibiting effect of water vapour on this reaction may be attributed to the competition between water and HCl for the active centres on the glass surface, and thus reducing the effective concentration of the latter. The retarding effect of nitrogen at higher pressures is attributed to a reduction in the rate of diffusion of the reactants from the body of the reaction vessel to the walls.

The following mechanism is suggested to explain the reaction :

$$N_2O_4 + 2 \text{ HCl (ads.)} \rightarrow H_2O (ads.) + \text{NOCl} + \text{NO}_2Cl, \quad (1)$$

$$NOCl + HCl (ads.) \rightarrow Cl_2 + HNO,$$
 (2)

$$HNO + N_2O_4 \rightarrow HNO_2 + NO + NO_2, \qquad (3)$$

$$NO + NO_2Cl \rightarrow NO_2 + NOCl,$$
 (4)

$$2NO + Cl_2 \rightarrow 2 NOCl,$$
 (5)

$$2 \operatorname{HNO}_2 \to \operatorname{H}_2\operatorname{O} + \operatorname{NO} + \operatorname{NO}_2. \tag{6}$$

The heterogeneous nature of step (1) has been discussed, and this step is ratecontrolling. Using the bond-dissociation energies given by Cottrell,¹² together with the value of 29.5 kcal for the dissociation energy of the NO₂—Cl bond found by Cordes and Johnston,¹³ it is found that reaction (1) is endothermic by about 4 kcal. To this must be added the difference between the heats of adsorption of HCl and H₂O on glass. If one assumes these to be about the same as the heats of condensation, and there is evidence that this is so for water,¹⁴ then reaction (1) would be endothermic to about 10 kcal and thus is energetically possible as the rate-controlling step.

Reaction (2) is analogous to the fast reaction NOCl + Cl \rightarrow NO + Cl₂ which is postulated by Burns and Dainton ¹⁵ as an intermediate step in the photochemical formation of phosgene in the presence of NOCl. These workers give the rate constant for this reaction as 10^{10.06} exp (-1060/RT) l. mole⁻¹ sec⁻¹. Energetically, reaction (2) should be similar, since the difference lies in the breaking of an H—Cl bond weakened by adsorption and the formation of the HN bond in HNO. Reaction (2) is thus also likely to be fast compared with reaction (1). Reaction (3) accounts for the disappearance of HNO and the formation of NO which is necessary for the overall stoichiometry. Reaction (4) has been investigated by Freeling, Johnston and Ogg,¹⁶ who find the rate constant to be 0.83 × 10⁹ exp (-6900/RT) l. mole⁻¹ sec⁻¹. This is again much larger than the overall rate constant for the reaction and thus no NO₂Cl will survive.

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Reaction (5) is again fast with a third-order rate constant of $1.7 \times 10^2 1.2$ mole⁻² sec⁻¹ at 27.5°C.¹⁷ Thus no nitric oxide would be found in the products. Reaction (6) has frequently been postulated in gas-phase reactions where nitrous acid is likely as an intermediate.^{18, 19}

One other possible reaction may be considered, viz.,

$$3 \text{ NO}_2 + \text{H}_2\text{O} \Rightarrow 2 \text{ HNO}_3 + \text{NO}_3$$

Forsythe and Giauque ²⁰ have calculated the equilibrium constant for this reaction as 2.8×10^{-3} atm⁻¹ at 52°. Thus for a mixture of 50 mm NO₂ and 10 mm H₂O, a pressure drop of ~1 mm would be expected at this temperature. However, on mixing 50 mm of NO₂ and 10 mm H₂O at 55°C (the temperature at which most of the kinetic runs were made), no appreciable change in pressure was observed over a period of 90 min. Thus this reaction is too slow to contribute appreciably to the reaction between nitrogen peroxide and HCl.

The low value of the pre-exponential factor, which corresponds to an entropy of activation of -21.4 cal/mole deg. at 55° is to be expected in view of the heterogeneous nature of the first step which involves the collision between a N₂O₄ molecule and two adsorbed HCl molecules.

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