Gas-Phase Reactions between Carbon Monoxide, Chlorine and Nitrogen Dioxide

BY J. H. THOMAS AND G. R. WOODMAN

Chemistry Dept., University College, Cardiff

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The reactions between carbon monoxide, chlorine and nitrogen dioxide have been studied over the temperature range 381-473°C by manometric and photometric methods. The kinetic equations for this system has been established, and the proposed mechanism leads to a velocity constant for the reaction, $COCl+NO_2 \rightarrow CO_2+NO+Cl$ of $k = 10^{8.84} \exp(+160 \pm 250/RT)$ l. mole^{-1} sec^{-1}.

George and Thomas [1] in studies of the reactions between chloromethanes and NO_2 at temperatures in the region 210-300°C found that CO_2 was an important product in the reaction between $CHCl_3$ and NO_2 but no CO_2 was found in the reaction between CH_2Cl_2 and NO_2. They suggested that CO_2 was formed by a reaction between COCl radicals (which are expected to occur in the $CHCl_3$ reaction) and NO_2, viz.,

$$COCl+NO_2 \rightarrow CO_2+NOCl.$$

This reaction was postulated although Rollefsen and Montgomery [2] had shown that the analogous reaction of oxygen

$$COCl+O_2 \rightarrow CO_2+ClO$$

did not occur above 200°C. The work presented here results from an attempt to verify the suggestion of George and Thomas.

COCl radicals were not generated by photolysis of phosgene, as in the work of Rollefsen and Montgomery, since photolysis of NO_2 would occur simultaneously. Thermal decomposition of phosgene is too slow to make it a profitable source of COCl radicals at temperatures of 500°C or less. The thermal reaction between CO and Cl_2 was therefore used as a source of COCl radicals at temperatures between 381 and 473°C.

EXPERIMENTAL

MATERIALS

Carbon monoxide was obtained from cylinders and purified by passing over asbestos wool at dull red heat (to remove any carbonyl impurities) and then through traps cooled in liquid air. Chlorine, obtained from cylinders, was purified by passing through silica gel and then by fractionation at −80°C. The preparation and purification of other gases have been described elsewhere.[3a, b]

APPARATUS

A conventional high-vacuum apparatus in Pyrex was used permitting both manometric measurement (by means of a glass spiral gauge) and photometric measurement of the NO_2 concentration.[4] Two cylindrical reaction vessels were used, vessel 1, diam 45 mm, volume 278 cm^3, surface area 280 cm^2, and vessel 2, which was packed with lengths of Pyrex tubing, volume 160 cm^3, surface area 1730 cm^2. Products were analyzed by vapour phase chromatography (a 12 ft. column of dimethyl phthalate on Celite 545) and infra-red spectrometry.

RESULTS

PRELIMINARY EXPERIMENTS

Nitrogen dioxide partially dissociates at the temperatures used in this work to form nitric oxide and oxygen $2NO_2 \rightleftharpoons 2NO + O_2$. This gas was therefore always admitted first to the reaction vessel and the composition of the mixture calculated from the final equilibrium pressure using the known equilibrium data.[5]

Carbon monoxide is oxidized by NO_2 at these temperatutes and Crist and Brown[6] found that for the reaction

$$CO + NO_2 \rightarrow CO_2 + NO. \qquad (1)$$

$$-d[NO_2]/dt = 10^{8\cdot 7} \exp(-27{,}800/RT)\,[CO]\,[NO_2] \text{ mole l.}^{-1} \text{ sec}^{-1}$$

over the temperature range 225-290°C. This work has been repeated over the range

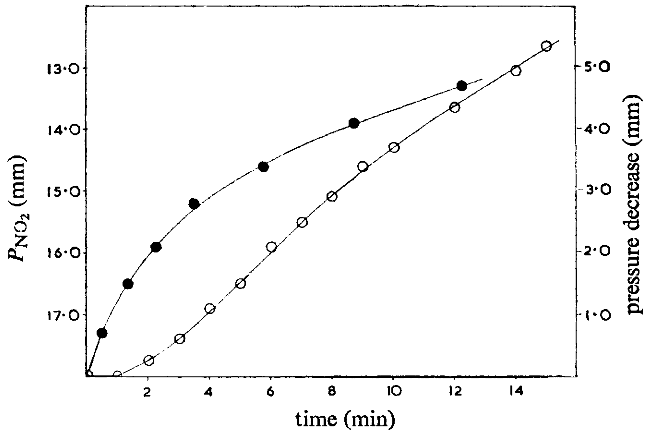

FIG. 1.—Typical reaction plots, $CO + NO_2$, $P_{CO} = 103\cdot 1$ mm, $P_{NO_2} = 18\cdot 0$ mm; temp. 393°C. ○, manometric measurements; ●, photometric measurements.

393-473°C and on the basis of the initial rate of reaction of NO_2, the photometric experiments give the result,

$$-d[NO_2]/dt = \\ 10^{8\cdot 8} \exp(27{,}700 \pm 400/RT)\,[CO]^{1\cdot 05 \pm 0\cdot 02}[NO_2]^{0\cdot 96 \pm 0\cdot 02} \text{ mole l.}^{-1} \text{ sec}^{-1}$$

in good agreement with earlier work. Fig. 1 shows typical plots of the change in NO_2 and total pressure with time. The latter plot shows a period of zero pressure change followed by a pressure decrease. Reaction (1) occurs with no pressure change and the observed change in pressure results from the reaction

$$2NO + O_2 \rightarrow 2NO_2. \qquad (2)$$

The agreement between the present work and that of Crist and Brown, and the absence of any pressure change in the early part of the reaction shows that initially the rate of reaction (2) is negligible compared with that of reaction (1).

A brief manometric study of the reaction

$$CO + Cl_2 \rightarrow COCl_2 \qquad (3)$$

showed that $d[COCl_2]/dt = [CO]^{0\cdot98\pm0\cdot01} [Cl_2]^{1\cdot55\pm0\cdot01}$ in agreement with the work of Bodenstein and Plaut.[7]

Further preliminary experiments showed that there was no measurable reaction over a period of 1 h at 393°C between (*a*) carbon monoxide and oxygen, (*b*) phosgene and nitrogen dioxide, (*c*) chlorine and nitrogen dioxide, and that (*d*) oxygen had no effect on the reaction between chlorine and carbon monoxide.

When NO and Cl_2 were mixed at this temperature the equilibrium:

$$2NO+Cl_2 \rightleftharpoons 2NOCl \tag{A}$$

was established so rapidly that no appreciable pressure change was observed, i.e., equilibrium was complete before pressure observations could be made. For this equilibrium

$$K_P = P^2_{NOCl}/P^2_{NO}P_{Cl_2} = 8\cdot044\times10^{-4}\ \text{mm}^{-1}\ \text{at}\ 393°\text{C}.^8$$

SYSTEM CO, Cl_2 AND NO_2

Appropriate amounts of CO and Cl_2 were premixed at room temperature in a darkened vessel and then admitted to the reaction vessel in which the equilibrium mixture of NO_2, NO and O_2 was already present. Typical reaction plots are shown in fig. 2. The rate at which NO_2 reacted was always greater in these systems than that found for a mixture of $CO+NO_2$ alone. Thus a reaction other than reaction (1) must be occurring. The sigmoid shape of the manometric plot is to be expected in a system where reactions (1), (2) and (3) are occurring and the photometric results are of more value in kinetic determinations.

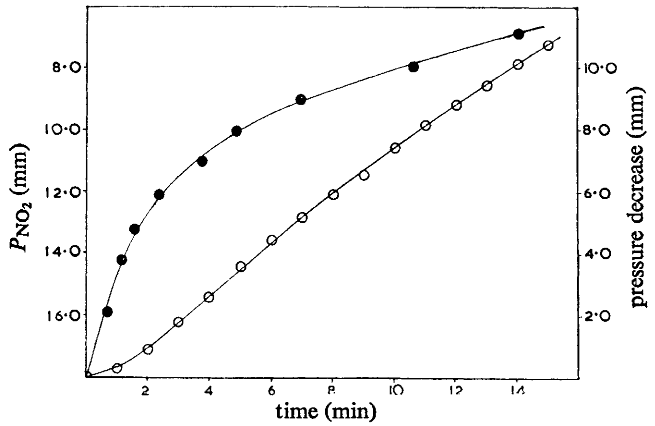

FIG. 2.—Typical reaction plots, $CO+NO_2+Cl_2$. $P_{CO} = 103\cdot2$ mm, $P_{NO_2} = 18\cdot0$ mm, $P_{Cl_2} = 104\cdot1$ mm; temp. 393°C.

ORDERS OF REACTION

Measurement of the initial rate of reaction of NO_2 (from photometric experiments) in a series of experiments in which the initial pressure of one of the reactants was varied and the pressures of the other two maintained at a constant value, were used to determine the kinetic orders in the three reactants. Plots of log (initial rate) against log (reactant pressure) are shown in fig. 3 (393°C). No allowance has been made for the small decrease in Cl_2 pressures due to the rapid establishment of equilibrium (A). The low value of the equilibrium constant means that in the most unfavourable case the error is less than 3 %. For CO the plot is linear the slope giving an order of 1·07±0·01 in CO. For Cl_2 the plot is curved, the " order " varying

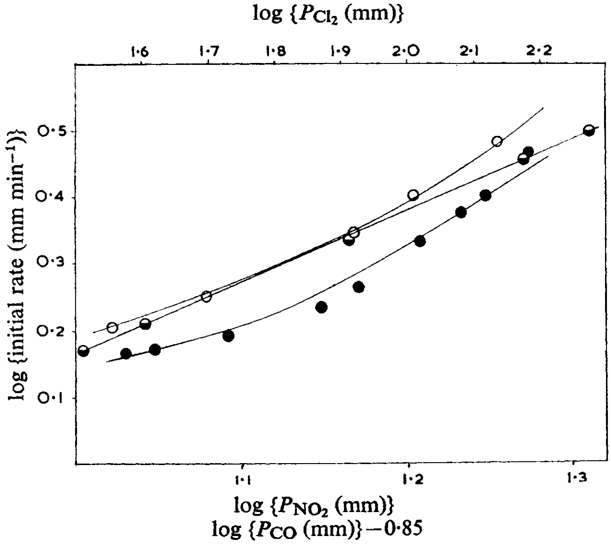

FIG. 3.—" Orders " of reaction at 393°C. ◐, order in CO; P_{Cl_2} = 104·3 mm, P_{NO_2} = 14·5 mm, ●, order in Cl_2; P_{CO} = 103·4 mm, P_{NO_2} = 14·5 mm, ○, order in NO_2; P_{CO} = 103·4 mm, P_{Cl_2} = 104·3 mm.

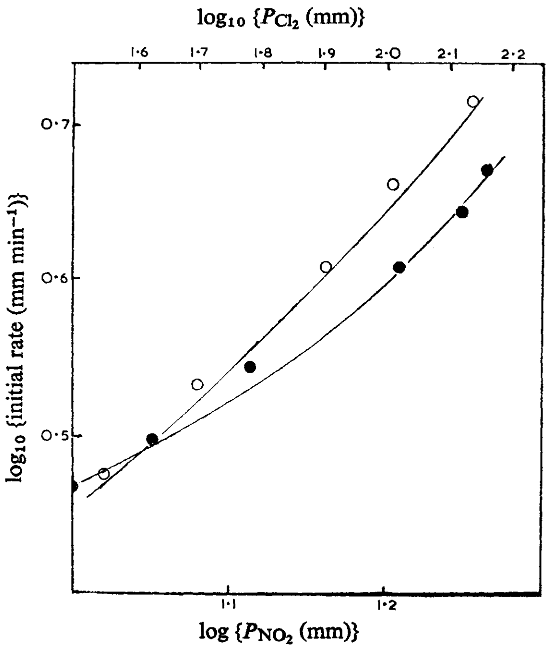

FIG. 4.—" Orders " of reaction at 420°C. ●, order in Cl_2; P_{CO} = 103·5 mm, P_{NO_2} = 14·5 mm, ○, order in NO_2; P_{CO} = 103·5 mm, P_{Cl_2} = 105·0 mm.

from 0·15 to 0·8 over the pressure range studied. For NO_2 the plot was again curved, the " order " varying between 1 and 1·7 in the example given (P_{CO} = 103·4 mm; P_{Cl_2} = 104·3 mm).

Since the latter two plots were curved an investigation of the effect of chlorine on the NO_2 order was made. A series of NO_2 " order " plots were therefore obtained in which P_{CO} = 103·4 mm but in successive determinations P_{Cl_2} had the values 0, 31·3, 53·9 and 103·5 mm. In all cases curved plots were obtained and all had a slope of 1 at low NO_2 pressures. At the highest NO_2 pressure used the gradient of the curve had the values 1·0, 1·2, 1·4 and 1·7, increasing with increasing chlorine pressure. These studies showed therefore (i) the order in CO = 1, (ii) the " order " in Cl_2 increases with increasing Cl_2 pressure, (iii) the " order " in NO_2 increases with increasing NO_2 pressure and with increasing Cl_2 pressure. Similar effects were found at 420°C (fig. 4).

EFFECT OF ADDITIVES

Nitric oxide was always present in the reaction mixture as a result of the decomposition of NO_2. By using suitable initial pressures of NO_2 and added NO it was possible to achieve an equilibrium mixture of NO and NO_2 in which the NO_2 pressure was constant but that of the NO varied. The addition of NO to the system in this way resulted in a significant change in the initial pressures of NO and Cl_2 as a result of equilibrium (A). In table 1 the necessary corrections have been made and the pressures of NO, Cl_2 and CO given are those following the establishment of equilibrium (A). The orders in CO and Cl_2 are both close to unity at the pressures used in these experiments and the product $P_{CO}P_{Cl_2}$ is constant. The decrease in rate can thus be attributed to the increasing NO pressure. The addition of up to 100 mm of CO_2 and up to 250 mm of N_2 had no appreciable effect on the reaction. The use of the packed reaction vessel was also without effect.

TABLE 1.—INHIBITION BY NO AT 393°C

P_{NO}(mm)	P_{Cl_2}(mm)	P_{NO_2} = 14·5 mm P_{CO}(mm)	$P_{CO}P_{Cl_2}$ (10^{-3} mm^2)	initial rate (mm min^{-1})
19·05	102·91	105·18	10·82	2·22
38·80	101·50	106·6	10·82	1·90
58·10	100·17	107·92	10·81	1·75
78·50	98·80	109·30	10·80	1·70

EFFECT OF TEMPERATURE

The initial rates of reaction for a mixture of P_{CO} = 103 mm, P_{Cl_2} = 104 mm and P_{NO_2} = 14·5 mm were measured over the temperature range 381-473°C. The resulting plot of log (initial rate) against $1/T$°K was linear with slope corresponding to an apparent activation energy of 19·7 kcal, i.e., much less than that found for the $CO+NO_2$ reaction (fig. 5).

ANALYSIS OF PRODUCTS

The products of the reaction were CO_2, NO, $COCl_2$ and NOCl with excess CO and Cl_2. All analytical experiments used excess CO and Cl_2 since NO_2 is difficult to estimate by gas chromatography. The NOCl found at room temperature in the products would be dissociated into NO and Cl_2 at the temperature of the reaction. This correction has been made in the typical analysis shown in table 2. The element and pressure balances are good.

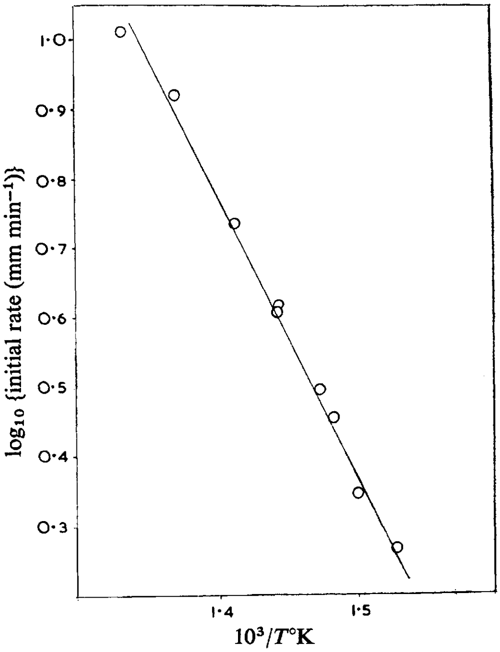

FIG. 5.—Effect of temperature. $P_{CO} = 103{\cdot}4$ mm, $P_{Cl_2} = 104{\cdot}3$ mm, $P_{NO_2} = 14{\cdot}5$ mm.

TABLE 2.—ANALYSIS OF PRODUCTS AT 393°C

initial reactants, mm	products, mm
$P_{CO} = 104{\cdot}0$	$P_{CO} = 26{\cdot}6$
$P_{Cl_2} = 105{\cdot}1$	$P_{Cl_2} = 66{\cdot}5$
$P_{NO_2} = 14{\cdot}5$	$P_{NO} = 39{\cdot}2$
$P_{NO} = 24{\cdot}6$	$P_{CO_2} = 39{\cdot}9$
$P_{O_2} = 12{\cdot}3$	$P_{COCl} = 38{\cdot}6$
	total $= 210{\cdot}8$

final reaction vessel pressure $= 209{\cdot}5$

DISCUSSION

INHIBITING EFFECT OF NITRIC OXIDE. Using the data of table 1, the plot of initial rate against $1/P_{NO}$ is linear with a positive intercept of 1·54 mm min^{-1} (fig. 6). This shows that the overall rate of reaction under these conditions has the form

$$\text{rate} = a + b/cP_{NO}, \tag{B}$$

where a, b and c are constants.

OVERALL RATE EQUATION. No two term expression gave an adequate representation of the kinetic results over the whole range of pressures studied. The best fit was obtained from the three-term expression

$$-dP_{NO_2}/dt = k_1P_{CO}P_{NO_2} + k_2P_{CO}P_{NO_2}P_{Cl_2}^{\frac{1}{2}} + k_3P_{CO}P_{NO_2}P_{Cl_2}/P_{NO} \tag{C$_2$}$$

In the absence of Cl_2 this reduces to the normal expression for the CO, NO_2 reaction, viz., $-dP_{NO_2}/dt = k_1P_{CO}P_{NO_2}$. At constant P_{CO}, P_{Cl_2} and P_{NO_2}, but varying pressures of NO, the equation has the form (B) above.

The first term in eqn. (C) represents the reaction between CO and NO_2 for which k_1 is known. k_2 and k_3 may then be calculated from a series of experiments in which P_{CO}, P_{NO_2}, P_{NO} and P_{Cl_2} are varied. The best fit to the experimental points is found for the following values of k_2 and k_3.

$$\text{At } 393°\text{C}, \; k_2 = 3{\cdot}66 \times 10^{-5} \text{ mm}^{-1{\cdot}5} \text{ min}^{-1},$$
$$k_3 = 5{\cdot}813 \times 10^{-6} \text{ mm}^{-2} \text{ min}^{-1}.$$
$$\text{At } 420°\text{C}, \; k_2 = 6{\cdot}62 \times 10^{-5} \text{ mm}^{-1{\cdot}5} \text{ min}^{-1},$$
$$k_3 = 1{\cdot}044 \times 10^{-5} \text{ mm}^{-2} \text{ min}^{-1}.$$

In calculating these values allowance has been made for equilibrium (A). Using these values the initial rates of reaction may be calculated for any mixture of CO, Cl_2, NO_2 and NO. The results of these calculations at 393 and 420°C are shown in fig. 6. The points shown are the experimental values of the initial rate and the solid lines represent theoretical curves based on the above values of k_2 and k_3.

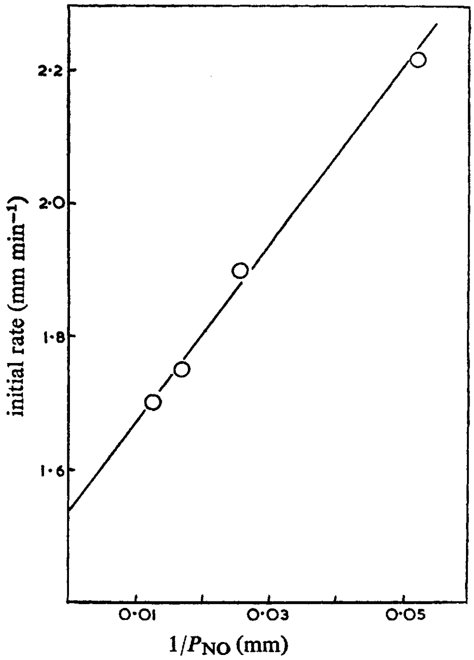

FIG. 6.—Inhibition by NO.

One final point in confirmation, was that the intercept of 1·54 mm min^{-1} (fig. 6) represents the rate to be expected when $P_{NO} = \infty$, i.e., the value of the rate when only the first two terms of eqn. (B) are considered. Using the value of k_2 at 393°C already given, the calculated intercept is 1·53 mm min^{-1} in good agreement with that found experimentally.

MECHANISM OF REACTION. The rate of reaction of NO_2 is greater when added to a mixture of CO and Cl_2, than when added to CO alone. For example, for a mixture

$P_{CO} = 103$ mm, $P_{NO_2} = 14{\cdot}5$ mm at 393°C, $-dP_{NO_2}/dt = 0{\cdot}96$ mm min^{-1}, but for a mixture $P_{CO} = 103$ mm, $P_{NO_2} = 14{\cdot}5$ mm and $P_{Cl_2} = 104$ mm, $-dP_{NO_2}/dt = 2{\cdot}15$ mm min^{-1}. It follows that a reaction of NO_2 other than $CO+NO_2 \rightarrow CO_2+NO$ is occurring. No reaction has been found between NO_2 and Cl_2 or $COCl_2$ and therefore NO_2 must be reacting with an intermediate in the system. Moreover, since the only products of reaction are CO_2, $COCl_2$ and NO, then NO_2 must react to form one or more of these products.

Bodenstein and Plaut [7] suggest the following mechanism for the thermal reaction between CO and Cl_2.

$$Cl_2 \rightleftharpoons 2Cl \tag{4}$$

$$CO+Cl \rightleftharpoons COCl \tag{5}$$

$$COCl+Cl_2 \rightleftharpoons COCl_2+Cl \tag{6}$$

$$COCl+Cl \rightarrow COCl_2. \tag{7}$$

The intermediates in this system are COCl and Cl.

The first possible reaction is therefore

$$COCl+NO_2 \rightarrow CO_2+NO+Cl. \tag{8}$$

Eqn. (4)-(8) lead to the kinetic expression

$$-d[NO_2]/dt = k_8K_5K_4^{\frac{1}{2}}[CO][Cl_2]^{\frac{1}{2}}[NO_2],$$

where K_5 and K_4 are the equilibrium constants for reactions (5) and (4). This is identical with the second term of eqn. (C), and k_2 in eqn. (C) $= k_8K_5K_4^{\frac{1}{2}}$. K_5 has been determined by Burns and Dainton [9] and K_4 is available.[10] Using these values with the values of k_2 given previously we find

$$k_8 = 8{\cdot}77\times10^8 \text{ l. mole}^{-1}\text{ sec}^{-1} \text{ at } 393°\text{C},$$

and

$$k_8 = 8{\cdot}47\times10^8 \text{ l. mole}^{-1}\text{ sec}^{-1} \text{ at } 420°\text{C}.$$

If allowance is made for the uncertainty in K_5 then k_8 may be expressed as

$$k_8 = 10^{8{\cdot}84} \exp(+160\pm250)/RT \text{ l. mole}^{-1}\text{ sec}^{-1}.$$

Reaction (8) is exothermic to the extent of 47 kcal, and a low activation energy is to be expected. k_6 has the values $2{\cdot}68\times10^8$ l. mole^{-1} sec^{-1} and $2{\cdot}92\times10^8$ l. mole^{-1} sec^{-1} at 393 and 420°C respectively.[8] Reactions (6) and (8) will therefore be competitive under the conditions of the present experiments.

The third term in eqn. (C) cannot be obtained by any simple modification of the Bodenstein mechanism for the carbon monoxide+chlorine reaction. Probably the higher order in NO_2 follows from the participation of NO_2 in the initiation step, e.g.,

$$2NO_2+Cl_2 \rightarrow 2NO_2Cl. \tag{9}$$

The concentration of NO_2Cl in an equilibrium mixture of NO_2, Cl_2 and NO_2Cl will be very small at these temperatures. Cordes and Johnston [11] find that the equilibrium constant for the reaction,

$$NO_2Cl \rightleftharpoons NO_2+\tfrac{1}{2}Cl_2 \tag{D}$$

is $13{\cdot}0$ mole$^{0{\cdot}5}$ cm$^{-1{\cdot}5}$ at 599°K and $\Delta H = -0{\cdot}09$ kcal. Thus, at 666°K, $K_{(D)} = 21{\cdot}8$ mole$^{0{\cdot}5}$ cm$^{-1{\cdot}5}$. For a mixture, $P_{NO_2} = 14{\cdot}5$ mm and $P_{Cl_2} = 104{\cdot}0$ mm, $P_{NO_2Cl} = 1{\cdot}6\times10^{-8}$ mole l.$^{-1}$. This, however, is 10 times the concentration of chlorine atoms resulting from the dissociation of 104 mm of chlorine at this temperature. It is therefore possible that NO_2Cl could act as a chain carrier, e.g.,

$$2NO_2+Cl_2\rightarrow 2NO_2Cl \tag{9}$$

$$NO_2Cl+CO\rightarrow CO_2+NO+Cl \tag{10}$$

$$NO_2+Cl\rightarrow NO_2Cl \tag{11}$$

$$NO_2Cl+NO\rightarrow NOCl+NO_2 \tag{12}$$

$$2NO_2Cl\rightarrow 2NO_2+Cl_2. \tag{13}$$

Reactions (9)-(13) lead to the kinetic equation,

$$-\frac{d[NO_2]}{dt}=\frac{2k_{10}k_9[NO_2]^2[Cl_2][CO]}{k_{12}[NO]+2k_{13}[NO_2Cl]}.$$

k_{12} has the value of $4{\cdot}5\times10^6$ l. mole^{-1} sec^{-1} at 393°C,[12] and Cordes and Johnston [11] find that the bimolecular rate constant for the reaction, $NO_2Cl\rightarrow NO_2+\frac{1}{2}Cl_2$, equals $5{\cdot}4\times10^4$ l. mole^{-1} sec^{-1} at this temperature. The second term in the denominator will be negligible under the conditions of the present work and the expression agrees with the third term of eqn. (C). This is not the only mechanism that can be written to satisfy this term, and NO_2Cl would be expected to be produced through the reaction

$$NO_2+NOCl\rightarrow NO_2Cl+NO \tag{14}$$

in addition to reaction (9). More precise details of the reaction between NO_2 and Cl_2 are required before a definite mechanism can be put forward.

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