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Decomposition of Nitrosyl Chloride on Glass and Quartz Surfaces

P. G. ASHMORE AND W. HERTL

From the Department of Physical Chemistry, University of Cambridge, England

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A study has been made of the heterogeneous decomposition of nitrosyl chloride on Pyrex and quartz surfaces. The activity of these surfaces after different treatments has been correlated with the presence of surface hydroxyl groups.

It is well known that the decomposition of nitrosyl chloride is reversible, and until recently the decomposition and recombination were assumed to proceed by the homogeneous molecular reactions (1) and (2). Experimental evidence has been found (*1, 2*) that at temperatures around 300°C a substantial part of the decomposition proceeds by another path, involving the slow formation of chlorine atoms by reaction (3) and their removal by the rapid reaction (6); there is a similar path for the recombination through reactions (5) and (4). In reactions (3) and (4) M′ represents any gas present.

$$2\,\mathrm{NOCl} \underset{(2)}{\overset{(1)}{\rightleftharpoons}} 2\,\mathrm{NO} + \mathrm{Cl_2}$$

$$\mathrm{NOCl} + \mathrm{M'} \underset{(4)}{\overset{(3)}{\rightleftharpoons}} \mathrm{NO} + \mathrm{Cl} + \mathrm{M'}$$

$$\mathrm{NO} + \mathrm{Cl_2} \underset{(6)}{\overset{(5)}{\rightleftharpoons}} \mathrm{NOCl} + \mathrm{Cl}$$

Under conditions where the recombination reactions can be ignored, this scheme leads to the following equation for the rate:

$$-d[\mathrm{NOCl}]/dt = \{k_1 + 2k_{3,\mathrm{NOCl}} + \textstyle\sum(2k_{3,\mathrm{M}}[\mathrm{M}]/[\mathrm{NOCl}])\}[\mathrm{NOCl}]^2$$

where M now represents any gas present other than nitrosyl chloride.

In the absence of added gases, however, Ashmore and Spencer (*1*) found evidence of a concurrent first order rate term which they represented as $\alpha[\mathrm{NOCl}]$. The velocity constant α was found to have an activation energy of 18 kcal mole^{-1}, far less than the activation energy of reaction (3) which is (*2*) about 35–37 kcal mole^{-1} for $\mathrm{M'} = \mathrm{NOCl}$, $\mathrm{N_2}$, NO, or $\mathrm{Cl_2}$. The additional rate was attributed to heterogeneous reactions on the wall (W) of the Pyrex reaction vessel, and α was identified with $2k_7$ (refers to reactions 7 and 11 of ref. *1*) assuming that the concentration $[\mathrm{Cl_W}]$ of chemisorbed chlorine atoms reaches a stationary state.

$$\mathrm{NOCl} + \mathrm{W} \xrightarrow{(7)} \mathrm{NO} + \mathrm{Cl_W}$$

$$\mathrm{NOCl} + \mathrm{Cl_W} \xrightarrow{(11)} \mathrm{NO} + \mathrm{Cl_2} + \mathrm{W}$$

In aged quartz vessels, however, the rate equation does not include (*2*) a first order term $\alpha[\mathrm{NOCl}]$.

These conflicting results have been explained by studies of the effect upon α of different treatments of vessel surfaces, of aging of the surfaces, and of changes in the surface–volume ratio. The rate term $\alpha[\mathrm{NOCl}]$ is certainly connected with reactions on the surfaces, and α can be taken as a measure of the activity of the surface for the decomposition of NOCl. The activity appears to be correlated with the surface concentration of hydroxyl groups. However, the surface reactions may not be as simple as (7) and (11).

EXPERIMENTAL

A conventional Pyrex glass vacuum apparatus for gas-phase kinetic studies was used for the preparation, purification, and storage of the gases and for delivering mixtures to the reaction vessel (*3*). Unpacked cylindrical vessels of Pyrex glass ($S/V = 1.4$) and quartz ($S/V = 1.4$), and three Pyrex glass vessels ($S/V = 16.5$, 6.8, and 3.0), constructed of concentric cylinders (*3*), were used. Various treatments of the surfaces are described with the results.

Mass spectrometric and gas chromatographic studies of the decomposition products of NOCl taken from a vessel with an active surface indicated that only traces of HCl, N_2O, or N_2 were formed and that the over-all decomposition is: $2\ \mathrm{NOCl} \rightarrow 2\ \mathrm{NO} + \mathrm{Cl_2}$.

The course of this decomposition, and the reverse combination, were followed by recording the pressure change with a pressure transducer (J. Langham Thomson Ltd. Type UP). The transducer was filled with Apiezon oil, type B (vapor pressure 10^{-7} mm Hg) in order to reduce the dead space and to protect the instrument from the corrosive reactants. The electrical controls for the transducer were similar to those described by Pratt (*4*). The transducer output was linear to within 1% and had a sensitivity sufficient to detect 0.005 mm Hg pressure change. Various checks were made at different times during the course of the investigation to ensure that negligible amounts of the reactants or products were dissolving in the tap grease or the Apiezon oil (*3*). For the formation of nitrosyl chloride, where much higher pressures of reactants were used, greaseless taps with fluorinated rubber diaphragms were used. The oil was isolated from the system with a cushion of nitrogen, which was satisfactory for the time needed to follow the course of a run (5 min).

RESULTS

The Decomposition Reaction

About 1200 decomposition runs were carried out. The runs were first analyzed by the equation used by Ashmore and Spencer (*1*).

$$-d[\mathrm{NOCl}]/dt = k'[\mathrm{NOCl}]^2 = \{k_1 + 2k_{3,\mathrm{NOCl}} + (2k_{3,\mathrm{M}}[\mathrm{M}]/[\mathrm{NOCl}]) + (\alpha/[\mathrm{NOCl}])\}[\mathrm{NOCl}]^2$$

If the terms $2k_{3,\mathrm{M}}[\mathrm{M}]$ and α are much smaller than 1/t (*a posteriori* it is known that this is true) the equation can be integrated (*3*) to give

$$\frac{1}{[\mathrm{NOCl}]} - \frac{1}{[\mathrm{NOCl}]_0} = \left\{k_1 + 2k_{3,\mathrm{NOCl}} + \frac{2k_{3,\mathrm{M}}[\mathrm{M}]}{[\mathrm{NOCl}]_0} + \frac{\alpha}{[\mathrm{NOCl}]_0}\right\} t = k''t$$

The slope of a plot of $[\mathrm{NOCl}]^{-1}$ against time for a given run gives k''. The slope of a plot of k'' against $[\mathrm{NOCl}]_0^{-1}$ for a set of runs in the absence of added gas M gives α, the velocity constant of the concurrent first order term. If a constant proportion of an inert gas M is mixed with the nitrosyl chloride, so that $[\mathrm{M}]/[\mathrm{NOCl}]_0$ is constant, plots of k'' against $[\mathrm{NOCl}]_0^{-1}$ are straight lines of the same slope as in the absence of M but displaced vertically by the amount $2k_{3,\mathrm{M}}[\mathrm{M}]/[\mathrm{NOCl}]_0$, as shown in Fig. 1 for $\mathrm{M} = \mathrm{N_2}$. Hence $k_{3,\mathrm{N_2}}$ was calculated. In the absence of inert gases in a vessel with no surface activity, the last two terms in the brackets above are zero, and the constant value of k'' is equal to $k_1 + 2k_{3,\mathrm{NOCl}}$; from the known value (*2*) of k_1, $k_{3,\mathrm{NOCl}}$ was determined at five temperatures. The Arrhenius parameters for $k_{3,\mathrm{NOCl}}$ and $k_{3,\mathrm{N_2}}$ were in good agreement with other results, as shown in Table 1.

TABLE 1

ARRHENIUS PARAMETERS FOR THE RATE CONSTANTS $k_{3,\mathrm{M}}$[a]

	This work		Other work	
$k_{3,\mathrm{M}}$	$\log_{10} A$	E	$\log_{10} A$	E
$k_{3,\mathrm{NOCl}}$	16.7	34.9	16.8	35.4 (*2*)
$k_{3,\mathrm{N_2}}$	16.2	35.2	16.3	35.2 (*2*)
$k_{3,\mathrm{Cl_2}}$	16.8	36.6	16.4	36.0 (*1*)

[a] A in $\mathrm{cm^3\ mole^{-1}\ sec^{-1}}$, E in $\mathrm{kcal\ mole^{-1}}$.

The values for $k_{3,\mathrm{Cl_2}}$ were determined at two temperatures using mixtures of chlorine and nitrosyl chloride in an inactive vessel. As shown in Table 1 the Arrhenius parameters agree with those found by Ashmore and Spencer (*1*). Their results, however, were obtained by a completely different method using the full equation for the rates later in the reaction when the back reaction cannot be ignored.

In vessels which had active surfaces, and with [M] = 0, the plots of k'' against $[\mathrm{NOCl}]_0^{-1}$ did not extrapolate to give the same intercept at $[\mathrm{NOCl}]_0^{-1} = 0$ as in the inactive vessels. (See, for example, the lowest plot in Fig. 1, where the horizontal dashed line shows the value of $k_1 + 2k_3$.) However, the agreement between results shown in Table 1 make it unlikely that the unexpected intercepts were due to errors in k'' arising, for example, from faulty calibration or from misinterpretation of the pressure recordings. Another possible cause of the low intercepts, a very fast initial reaction, was eliminated by constructing a small mixing vessel and checking the expected and actual pressures after sharing (a) nitrogen alone, and (b) nitrosyl chloride alone, into an active reaction vessel. There was also evidence that in some active vessels the total rate at higher pressures falls slightly below that in inactive vessels. The effect is small; if it is real, and not due to experimental errors, it can only be ascribed to a rapid heterogeneous component of the reverse combination reaction.

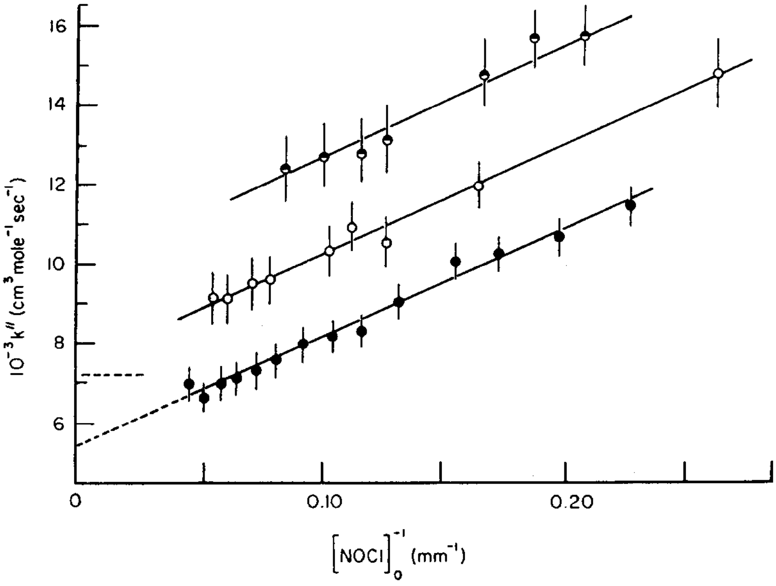

FIG. 1. Second order rate constant k'' vs $[\mathrm{NOCl}]_0^{-1}$ at 293°C in Pyrex vessel $S/V = 16.5$ for pure NOCl (●), with 75% N_2 (○) and with 86% N_2 (◓). The dashed line shows the value of $k_1 + 2k_3$.

Treatment of the Vessel Surface

Vessels treated by soaking in 60% nitric acid, washing with distilled water, and baking out *in vacuo,* showed high initial values of α which fell slowly over a period of weeks with successive experiments. The activity declined approximately exponentially with time, towards a "settled" value for each vessel and temperature. With settled surfaces, three Pyrex glass vessels with surface-to-volume ratios of 16.5, 6.8, and 1.4, and the quartz vessel with 1.6, showed an approximately linear relationship between α and the surface-to-volume ratio (Fig. 2).

The values of α for the various active, settled surfaces were plotted on an Arrhenius diagram, as shown in Fig. 3. The activation energy for the decomposition on all the surfaces seems to be the same,

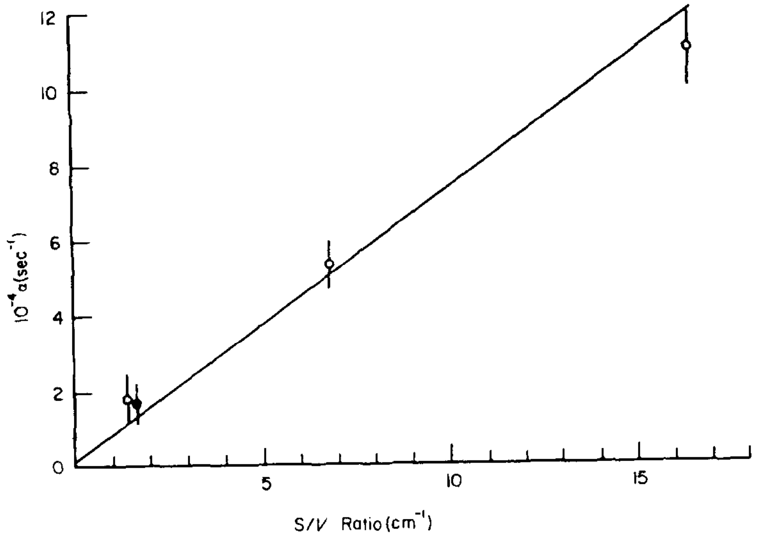

Fig. 2. Surface activity α at 300°C vs S/V ratio for Pyrex (○) and quartz (●).

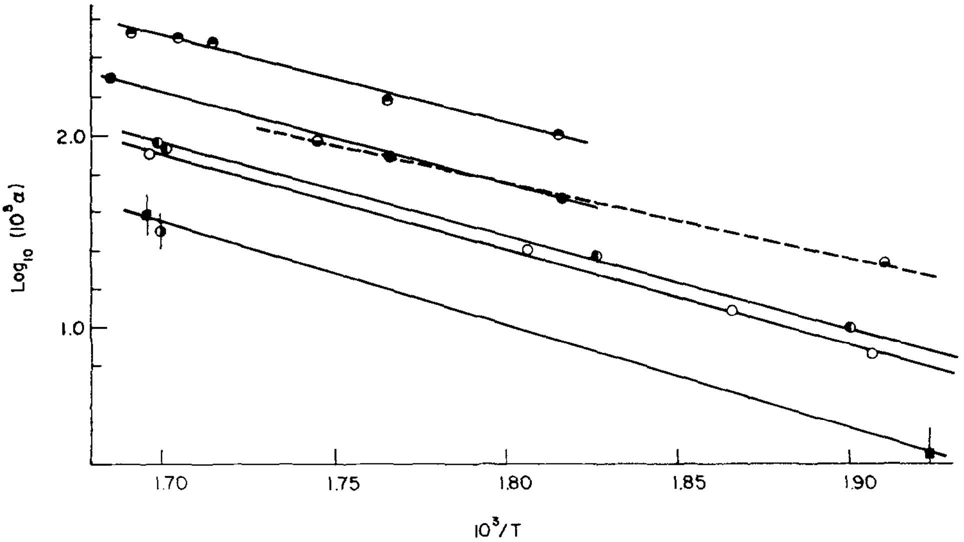

Fig. 3. Arrhenius plot for α in quartz (■), Pyrex $S/V = 1.4$ (ф), Pyrex $S/V = 6.8$ (○), Pyrex $S/V = 16.5$ (●), Pyrex $S/V = 1.4$ with first ◐ and second (◓) Na_2CO_3 treatment, and in other work (*1*) (⊖).

within the experimental error, the variable rates being due solely to changes in the pre-exponential factor. This strongly suggests that the same mechanism is operating on all the surfaces.

When a reaction vessel was soaked in a saturated solution of sodium carbonate, followed by rinsing with hot distilled water and baking *in vacuo*, the surface activity was lower than in a fresh "nitric acid" vessel, but higher than in a settled "nitric acid" vessel, and the activity did not fall with time; however, although it did not change, the actual level of activity was not the same after successive treatments with sodium carbonate.

Further treatment of settled "nitric acid" or "sodium carbonate" vessels with nitric acid always enhanced the surface activity.

Exposure of a surface of moderate activity to oxygen, water vapor, hydrogen chloride, chlorine, or nitrosyl chloride at the operating temperature had little effect. In contrast, exposure to chloroform vapor gave an almost inactive surface.

A very high activity on quartz was reduced to that of a settled quartz surface by flaming to an incipient red heat *in vacuo*. When quartz surfaces were heated to a brilliant white heat, the surface activity was completely destroyed (Fig. 4).

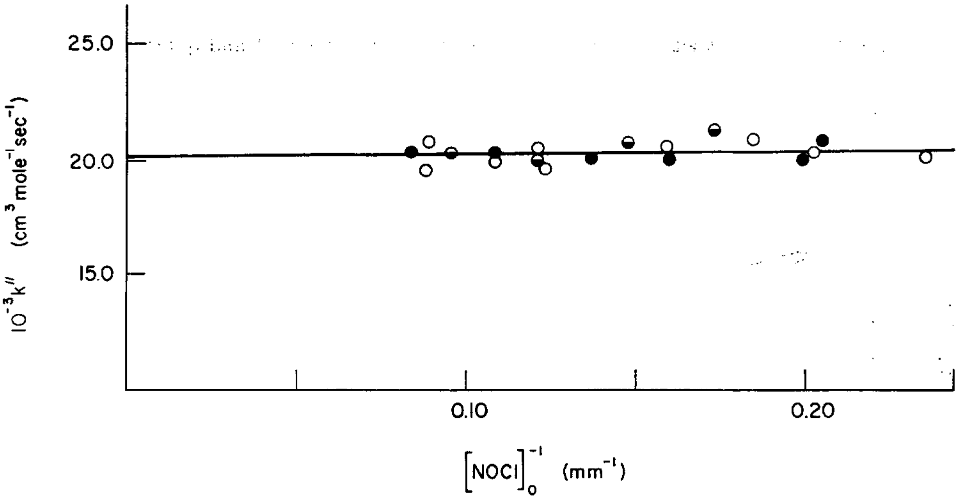

FIG. 4. Second order rate constant k'' vs $[NOCl]_0^{-1}$ at 317°C in a violently flamed vessel (○) and in the same vessel after exposure to water vapor for 1 hr ◒ and for 16 hr (●).

A completely inactive surface was reactivated by soaking with water, nitric acid, sodium nitrate, or sodium carbonate solutions. It was *not* reactivated by exposure overnight to water vapor at the temperature of the experiment (Fig. 4). When an inactive surface was allowed to stand for several weeks at room temperature it acquired a low activity.

Completely inactive surfaces were also prepared by fusing a thick even coating of sodium chloride on the surface.

TABLE 2
REPRESENTATIVE VALUES OF 10^4 α (SEC^{-1})

A. With 60% HNO_3, after 5 days use	1.2
B. A after 24 mm water vapor overnight	2.3
C. B after repeated evacuations	1.2
D. A after liquid water for 2 hr	104
E. D after 3 days use	21
F. E after 60% HNO_3	136
G. F after flaming 1 hr *in vacuo*	1.6
H. G after flaming to white heat	0

Some values of α (in sec^{-1}), corrected to unit S/V ratio and to 300°C, are shown in Table 2 for quartz surfaces with different treatments. For comparison, the value of $(k_1 + 2k_{3,NOCl})$ [NOCl] with 10 mm Hg of NOCl at 300°C is 28×10^{-4} sec^{-1}.

The common factor for high activity seems to be hydration of the surface. Dehydration of the surface appears to reduce the activity. It seems likely that the dehydration leads to a reduction of the concentration of hydroxyl groups on the surface, and this in turn to a reduction of active sites on the surface.

Parallel studies of the effect of surface treatments were carried out by treating porous silica samples in the same way as the reaction vessels, and examining the infrared spectra of the samples. The changes observed showed that the concentration of surface hydroxyl groups is reduced by heating, the reduction being greater the more severe the heating or the longer the exposure, and that the surface concentration can be substantially restored by further treating the heated surfaces with nitric acid. When treated with sodium carbonate, the hydroxyl concentration was quite low, but higher than a sample which had been soaked in nitric acid and heated at about 750°C. Similar changes have been observed previously by Young (*5*) and by de Boer and Vleeskens (*6*), while Hockey and Pethica (*7*) showed that the number of OH groups reaches a stable equilibrium value depending on the temperature, the value being close to zero at 900°C.

There is thus a close parallel between change in surface activity and changes in the surface OH concentration.

To see if there was any interaction between the surface hydroxyl group and any of the species present in the reaction mixtures some spectra were taken (Perkin-Elmer model 21) of a thin disc pressed from powdered silica (Cab-O-Sil H5) in the presence of nitric oxide, chlorine, and a mixture of nitric oxide and chlorine. In all cases the cell was heated to 350°C before the spectra were taken. The gas-phase spectra were also taken. With nitric oxide and chlorine only slight changes in the spectra commensurate with the background noise level were noted. With nitrosyl chloride present (from the nitric oxide + chlorine mixture) the N–O stretching frequency of nitrosyl chloride at 1800 cm^{-1} was perturbed towards the high frequency end of the spectrum, the broadening being of the order of +50 cm^{-1}, and the OH stretching frequency at 3750 cm^{-1} was perturbed toward the lower frequency end of the spectrum by about —150 cm^{-1}. The cell was allowed to stand for 2 days before another spectrum was taken. The spectrum was the same except for the appearance of some weak bands due to HCl and N_2O. The HCl may come from slow reactions of NOCl or of Cl_2 with surface OH groups or with tap grease, a point to be further investigated; the small amount of N_2O may come from reactions of NO on surface OH groups (*8*). There was comparatively little change in the height of the OH peak.

The sample cell was then evacuated. As shown in Fig. 5, the OH band with about 0.5 mm of gas left (curve A) is broader than after continued pumping at 7 × 10^{-4} mm Hg (curve B) at room temperature. The width is further decreased by continued pumping to 3 × 10^{-5} mm Hg (curve C) at 350°C, although the hydroxyl peak was still not reduced to its original width for the sample.

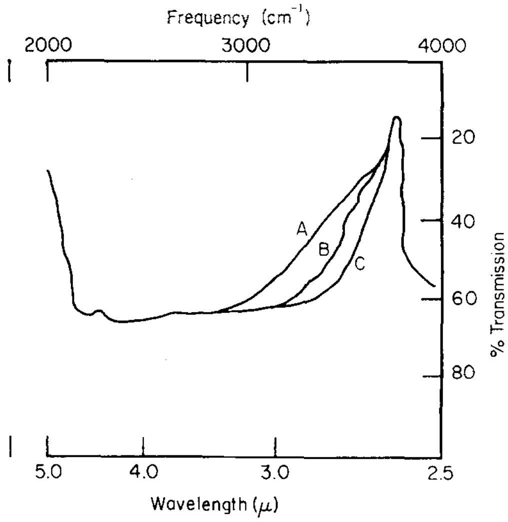

FIG. 5. Effect on OH band of evacuating A, to about 0.5 mm at 20°C; B, to about 7 × 10^{-4} mm Hg at 20°C; and C, to about 3 × 10^{-5} mm Hg at 350°C.

It appears, therefore, that only the adsorption of nitrosyl chloride is important. Negative shifts of the OH frequency have been observed with hydrogen bonding (*9*). Positive shifts of the NO stretching frequency have been observed for nitrosyl chloride dissolved in polar solvents (*10*). The perturbations of the OH and NO stretching frequencies would be in keeping with the hydrogen bonding of the N in NOCl to the H of the OH group. However, it is also possible that NOCl (or the group O=N— from NOCl) is adsorbed on sites (O or Si atoms) next to OH groups, and that hydrogen bonding occurs between N atoms and OH groups. The chief reason for suggesting this is that hydrogen bonding is unlikely to lead to appreciable adsorption at 350°C. The slow removal of an adsorbed species, shown by the slow decrease in the OH broadening, points to stronger bonds with the surface than hydrogen bonds.

The Combination Reaction

Some experiments were made on the combination reaction with the aim of investigating the effect on it of the surface treatments. Ashmore and Spencer (*1*) showed that chlorine atom reactions are very important in the early stages of the combination reaction at temperatures above 200°C, and devised plots of the experimental results which could be used to determine the velocity constant of the reaction

$$\mathrm{Cl} + \text{wall} \xrightarrow{10} \mathrm{Cl_w}$$

Using the same method, it was found (*3*) that a nitric-acid-soaked Pyrex vessel, a nitric-acid-soaked quartz vessel, and a violently flamed quartz vessel all had about the same activity per unit area at about 200°C, as well as having about the same values of k_{10} per unit S/V ratio as Ashmore and Spencer's vessel (see Table 3).

TABLE 3
VALUES OF k_{10} PER UNIT S/V

Vessel	Treatment	10^{-3} k_{10} per unit S/V (sec^{-1})
Pyrex	Acid soaked	1.3 ± 50%
Pyrex	Ashmore & Spencer[a]	1.1
Quartz	Acid soaked	2.6
Quartz	Violently flamed	1.9

[a] Reference 1.

Both these results suggest that reaction (10) (ref. *1*) which is rapid, is not very sensitive to treatment of the surface, in contrast with the surface decomposition reactions (see Table 2). Ogryzlo (*11*) found that chlorine atoms recombine rapidly on clean and coated Pyrex or quartz surfaces, except when the tubes were coated with certain acidic "poisons."

CONCLUSIONS

(1) A heterogeneous decomposition of nitrosyl chloride occurs at 250–350°C on Pyrex or quartz surfaces that have been activated by soaking in water or aqueous solutions.

(2) On these active surfaces the heterogeneous rate is substantial compared with the homogeneous rate at low pressures ($\leqslant$ 10 mm Hg) of nitrosyl chloride in vessels of unit S/V ratio.

(3) The activity falls slowly with successive experiments to a "settled" value at each temperature.

(4) The activity is rapidly reduced by heating and the quartz surfaces can be completely inactivated by very strong flaming *in vacuo*.

(5) The surfaces with reduced activity can be reactivated by soaking with aqueous solutions, and, to a less extent, by exposure to water vapor. The completely inactive surfaces can also be reactivated by soaking with water but not by exposure to water vapor.

(6) The activation energy of the surface reaction is about 22 kcal mole^{-1} and is nearly independent of the absolute activities of the settled surfaces. Changes in activity thus appear to be due to changes in the concentration of active sites on the surface.

(7) There is spectroscopic evidence for changes in the surface concentration of OH radicals which parallel the changes in surface activity after different treatments. It seems likely that the active sites on the surface in heterogeneous decomposition are related to the OH groups present.

(8) There is spectroscopic evidence for the adsorption of nitrosyl chloride, or its fragments, but not of adsorption from nitric oxide gas or chlorine gas. The adsorbed nitrosyl chloride or its fragments interact with surface OH groups and are only slowly removed by pumping at elevated temperatures.

(9) The treatments which markedly

alter the rate of the heterogeneous decomposition have little effect on the adsorption of chlorine atoms in the combination reaction.

DISCUSSION

The heterogeneous decomposition of nitrosyl chloride on Pyrex or quartz appears to be closely linked with the presence of —OH groups. It is unlikely, however, that the reaction is solely between nitrosyl chloride and surface —OH groups. In the first place, the products of decomposition in the active vessels are almost exclusively nitric oxide and chlorine, and only with extended exposure to large silica surfaces are small quantities of HCl and N_2O formed. Secondly, from the value of α in settled vessels (Table 2), it can be shown that about 4×10^{14} molecules of NOCl would be decomposed each second with 10 mm Hg of NOCl in a vessel of S/V ratio unity at 300°C. The number of OH groups on unit surface (*7*) is about $1–2 \times 10^{14}$ cm^{-2}, so that the surface would rapidly be stripped if the major reaction is with OH groups. The heterogeneous decomposition persists for many runs, each of many seconds. It must be regarded as a surface-catalyzed reaction occurring on or near OH groups.

The spectroscopic evidence on the adsorption of nitrosyl chloride shows that the NOCl molecule is adsorbed and interacts with the OH groups. This, and the absence of effect of changing the OH concentration on the reaction of $Cl + W \rightarrow Cl_W$, suggests that the reactions originally proposed (*1*) must be modified.

$$NOCl + W \rightarrow NO + Cl_W$$
$$NOCl + Cl_W \rightarrow NO + Cl_2 + W$$

The stoichiometry of the complete reaction requires that two nitrosyl chloride molecules be linked with each surface reaction, assuming that products do not accumulate on the surface during the reaction. The heterogeneous reaction can thus be written in two steps

$$(i) \qquad NOCl + W \rightarrow NOCl_W$$

followed by

$$(iia) \quad NOCl + NOCl_W \rightarrow 2NO + Cl_2 + W$$

or

$$(iib) \quad NOCl_W + NOCl_W \rightarrow 2NO + Cl_2 + 2W$$

without specifying for the moment whether $NOCl_W$ represents a chemisorbed NOCl molecule or fragments such as NO_W and Cl_W.

It is easy to show (*3*) that nearly every gas-phase NOCl molecule with the requisite activation energy (22 kcal) which hits the wall must react in order to give the observed heterogeneous reaction rate in settled vessels. If (*ii*a) is the rate-determining step, the surface must in addition be nearly saturated with $NOCl_W$ to give the observed order (first) of the surface reaction and to account for its absolute rate. Treating the adsorption as NOCl + OH site $\rightleftharpoons NOCl_W$ it is possible to estimate the heat of adsorption required to give a high saturation at 300°C. Assuming that $NOCl_W$ is immobile but has the same internal partition functions as gaseous NOCl, the heat of adsorption for 90% coverage is about 28 kcal/mole. It would then be impossible for the NOCl to be bonded to the surface by hydrogen bonds, and necessary for the chemisorption to involve NO_W or Cl_W or both.

It is very unlikely that (*ii*b) is the rate-determining step. To give first order kinetics with (*ii*b) $[NOCl_W]$ must be proportional to $[NOCl]^{1/2}$. This could only occur with dissociative adsorption at low coverage, and low coverage is incompatible with the observed rates and activation energy.

It is, however, possible for (*i*) to determine the rate on a partially covered surface, the actual coverage being controlled by the relative rates of (*i*) and (*ii*a) plus any spontaneous desorption of NO_W and Cl_W. It would be necessary (and indeed seems very likely) for (*ii*a) to have a fairly substantial activation energy to give coverages sufficient for any effect of the adsorbed species to be seen spectroscopically.

The observations that in some very active vessels the total rate at higher pressures falls *below* the total rate in completely inactive vessels, and the associated observation that in many active vessels the extrapolated rates as $[NOCl]^{-1}$ tends to zero are lower than the rates in completely inactive vessels, are puzzling. They appear not to be due to experimental error, although it would be helpful to have them tested under different experimental conditions. Mechanisms can be devised which reduce the free atom path for the forward reaction, but they all require marked curvature of plots like these in Fig. 1 and there is no experimental evidence for such curvature.

Further studies by infrared spectroscopy of the adsorbed species during reaction are now being undertaken, with the aim of identifying the rate-determining step of the heterogeneous decomposition on silica. When this is done, the velocity constant α can be related to specific surface reactions.

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