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MASS SPECTROMETRIC STUDY OF THERMAL DECOMPOSITION OF OXALYL

CHLORIDE AT LOW PRESSURES

V. N. Khabashesku, B. Pödör,   UDC 543.51:541.11:542.92:546.
T. Székely, A. K. Mal'tsev,   264'131-31
and O. M. Nefedov

Processes of reductive chlorination of metal oxides, used to extract metals in the form of volatile chlorides are of great practical importance [1, 2]. In these processes, the thermal decomposition of the chlorinating agent itself has a major influence on the process rate. The chlorinating agents most frequently used are Cl_2 and mixtures of Cl_2 with CO, and $COCl_2$ is also used [2-4]. Research is going forward on new chlorinating agents such as CCl_4, C_2Cl_4, and others [2, 5-7]; another promising agent is oxalyl chloride [8].

Previously, on the basis of a kinetic analysis of the thermal decomposition of $(COCl)_2$ at atmospheric pressure, it was suggested that this reaction proceeds with the intermediate participation of the COCl radical and that it is a chain reaction [8]. However, in an investigation of the products from the thermal dissociation of $(COCl)_2$ under vacuum by means of matrix IR spectroscopy [9], neither the COCl radical nor any other unstable species were detected, which indicated that under these conditions, oxalyl chloride decomposes not through the radical mechanism (1) but through the molecular mechanism (2).

$$(COCl)_2 \xrightarrow{\Delta} \begin{cases} \xrightarrow{-\times\to} COCl + COCl \\ \longrightarrow CO + COCl_2 \end{cases}$$

$$\text{(1)}$$
$$\text{(2)}$$

Nonetheless, the possibility remained that unstable intermediate species might be formed in concentrations too low to be detected by IR spectroscopy. In the present work, therefore, the mechanism of $(COCl)_2$ pyrolysis at low pressures was investigated by means of a more sensitive mass spectrometric technique.

EXPERIMENTAL

The oxalyl chloride, 99% pure (GLC), was pyrolyzed in an electrically heated quartz tube reactor with a vacuum-tight connection to the ion source of a Balzers QMG-101 quadrupole mass spectrometer. The mass spectra were measured over the mass interval 0-200 with an instrument resolution of 150-200. The length of the pyrolysis tube was 70 mm, inside diameter 0.2-1 mm; the distance from the exit opening of the reactor to the cathode of the ion source was 10 mm. The temperature in the pyrolysis zone was measured with a Chromel—Alumel thermocouple and a Chinoin LP-839 indicating digital millivoltmeter to within ±1°C. The pressure in the pyrolysis zone was varied from $1\cdot10^{-3}$ to $1\cdot10^{-2}$ torr, and the temperature from 25° to 900°C. When the $(COCl)_2$ was diluted with argon in a 1:100 ratio, the total pressure in the reactor amounted to $2\cdot10^{-3}$ to $2\cdot10^{-1}$ torr.

DISCUSSION OF RESULTS

In Fig. 1 we show the mass spectra of $(COCl)_2$ in the interval of mass numbers up to 100, and also the mass spectrum of the pyrolysis products obtained at 800°C. Both spectra were obtained with a pressure of $5\cdot10^{-6}$ torr in the ionization chamber of the mass spectrometer. An analysis of these spectra indicates that the conversion of $(COCl)_2$ in pyrolysis is conveniently rated by the change in intensity of the peak of the ion $C_2O_2^{+\cdot}$ with m/z 56, which is formed by fragmentation of $(COCl)_2$ and is absent in the mass spectra of the presumed products
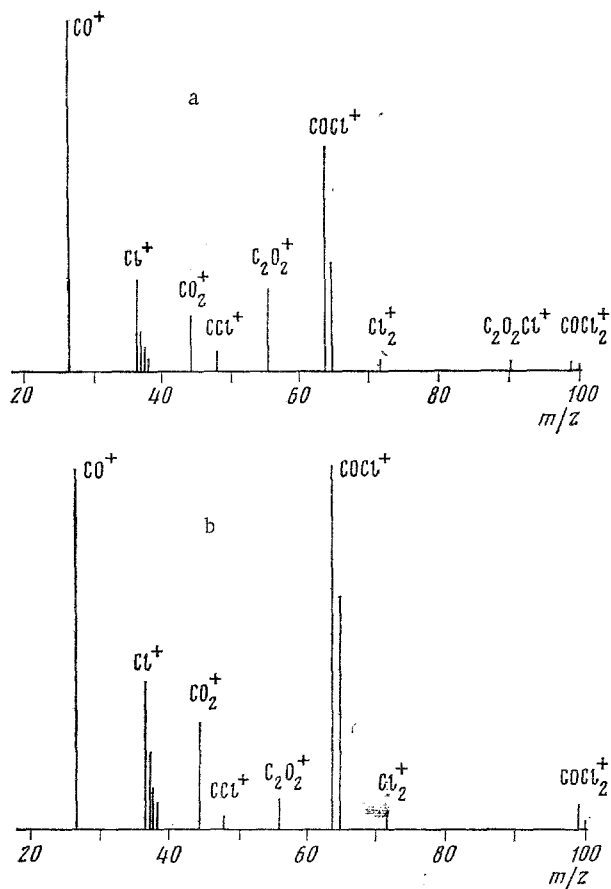
Fig. 1. Mass spectra: a) $COCL_2$; b) products of pyrolysis of $(COCl)_2$ at 805°C.
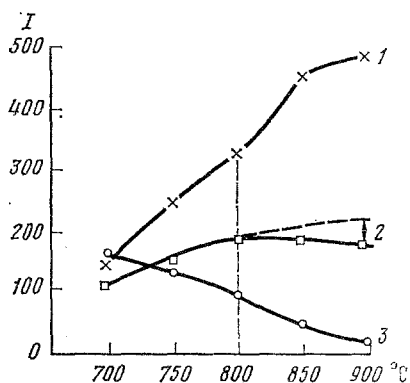

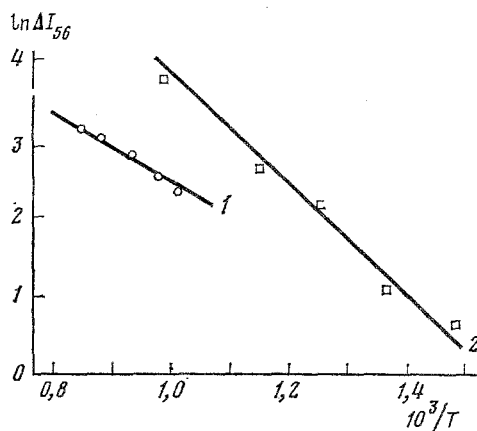Fig. 2   Fig. 3

Fig. 2. Temperature dependence of ion peak intensities characterizing: 1) CO (I_{28}); 2) $COCl_2$ (I_{63}); 3) $(COCl)_2$ ($I_{56}\cdot10$).

Fig. 3. Temperature dependence of peak intensity of ion with m/z 56, on Arrhenius coordinates.

of its pyrolysis — $COCl_2$ and COCl. The intense peak with m/z 28 (Fig. 1b) corresponds to the ions $CO^{+\cdot}$, which are formed by fragmentation of the molecular ions $(COCl)_2^{+\cdot}$ and $COCl_2^{+\cdot}$, and also by ionization of CO molecules. The second most intense peak, with m/z 63 (Fig. 1b) corresponds only to fragment ions $COCl^{+\cdot}$, formed by dissociative ionization of $(COCl)_2$ and $COCl_2$, since the sum of the calculated intensities of the peaks of these ions is exactly equal to the observed intensity of the peak with m/z 63. Thus, any contribution to the in-

TABLE 1. ntensities (in arbitrary units) of Fragment Ion Peaks in Mass Spectra of Products from $(COCl)_2$ Pyrolysis

T., °C	$(COCl)_2$					$COCl_2$ a*			CO†
	I_{28}	I_{56}	I_{63}	I_{98}	conversion, %	I_{63}	I_{98}	conversion, %	I_{28}
25	243‡	25,5	173	1,5	0	0	0	0	0
700	311	17,4	232	3,6	31,8**	114,0	2,6	0	145,2
756	379	13,5	245	5,0	47,1	153,0	4,2	0	250,4
805	409	9,4	262	5,7	63,1	198,2	5,2	0	319,4
852	496	5,3	225	5,4	79,4	189,4	5,1	4,5	446,0
903	449	3,0	200	5,0	88,4	180,0	4,8	10,0	420,9

*After deducting contribution of ions with m/z 63 and 98 formed by fragmentation of $(COCl)_2$.

†After deducting contribution of ions with m/z 28 formed by dissociative ionization of $(COCl)_2$ and products of its pyrolysis — $COCl_2$.

‡After deducting contribution of N_2^+ ion from background.

**Conversion of $(COCl)_2$ was determined from change in peak intensity for the ion with m/z 56.

tensity of this peak from the ionization of the COCl radical, the intermediate formation of which in the thermal decomposition of $(COCl)_2$ was proposed previously [8], was not found in the present work.

In Fig. 2 we show curves for the temperature dependence of the ion peak intensities characterizing the instantaneous concentrations of the original $(COCl)_2$ and products of its decomposition in the 700-900°C interval. It will be noted that the decrease in the intensity of the peak for the ion with m/z 56, which characterizes $(COCl)_2$, is accompanied by an increase in the intensity of the peak with m/z 28, illustrating the accumulation of CO in the course of the reaction, and an increase in the peak with m/z 63, characterizing the concentration of phosgene. Above 800°C, thermal decomposition of phosgene is observed, with the formation of additional quantities of CO and Cl_2; this corresponds to the bend of the curves in Fig. 2 and a decrease in intensity of the peaks of the $COCL_2^{+\cdot}$ ions (Table 1). When the pressure in the pyrolysis zone was increased from $1 \cdot 10^{-3}$ to $2 \cdot 10^{-1}$ torr at a constant temperature of 700°C, no changes were observed in the intensity ratio I_{56}/I_{63}. In this case also, no additional contribution to the peak with m/z 63 from the COCl radical could be detected.

Thus, the mass spectrometric data that were obtained by varying the conditions in the reaction zone support the previous conclusion [9] that the thermal decomposition of oxalyl chloride at low pressures proceeds through a molecular mechanism in accordance with Eq. (2) without the formation of the COCl radical.

The apparent activation energy of reaction (2) under the particular conditions studied (heterogeneous decomposition of oxalyl chloride on the wall) was estimated on the basis of the temperature dependence of $(COCl)_2$ conversion on Arrhenius coordinates. The value obtained from the slope of line 1 in Fig. 3, $E_{app} = 48 \pm 4$ kJ/mole (11.5 ± 1 kcal/mole), is substantially smaller than the values given in [8], 38.3 kcal/mole. Such a great difference in the values obtained for the activation energy is related to the chain character of thermal decomposition of $(COCl)_2$ that was observed at atmospheric pressure and with bimolecular collisions under homogeneous conditions [8]. The lower value of the activation energy that we have found is apparently related to realization of a monomolecular mechanism for the reaction taking place on the wall of the quartz reactor.

With the aim of determining the influence of the reactor surface on the process, we performed additional experiments in which mass spectra were obtained for the products from pyrolysis of $(COCl)_2$ when the original compound was diluted with Ar in a 1:100 ratio. In this case, the thermal decomposition of $(COCl)_2$ proceeded by collisions of "hot" Ar atoms with $(COCl)_2$ molecules in the gas phase. The higher value of the activation energy that was obtained under these conditions, 70 ± 12 kJ/mole as determined from the slope of line 2 in Fig. 3, indicates a significant contribution of chemisorption on the quartz reactor to the energetics of heterogeneous decomposition of $(COCl)_2$.

CONCLUSIONS

1. According to mass spectrometric data, the decomposition of $(COCl)_2$ at low pressures proceeds through a molecular mechanism with the formation of CO and $COCl_2$ without the intermediate formation of any sort of unstable species; this is in accord with results obtained previously by the use of matrix IR spectroscopy.

2. The apparent activation energy of heterogeneous decomposition of $(COCl)_2$ has been evaluated, and the significant role of chemisorption on the reactor surface has been established.

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SPATIAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES. 31.*

2-DIALKYLAMINO-1,3,2-DIOXAPHOSPHORINANES WITH FOUR-COORDINATED

PHOSPHORUS

B. A. Arbuzov, R. P. Arshinova,
V. N. Nabiullin, A. V. Il'yasov,
R. N. Gubaidullin, and T. D. Sorokina

UDC 541.63:547.1'118

Studies of the conformational behavior of various nonmethylated [2] and 4-methyl-substituted 2-dialkylamino-2-oxo-1,3,2-dioxaphosphorinanes (DOP) [3] gave the impetus for similar studies of thiophosphoryl derivatives with the aim of determining the relationships involved in the spatial structure of this class of compounds. For most of the previously studied 2-X-2-oxo-DOPs and their thiophosphoryl analogs, complete correspondence was found for the preferred conformations [4]. Differences can apparently be found in those few cases in which the compounds exist in the form of conformational equilibria, such that small changes such as the replacement of the phosphoryl group by thiophosphoryl can shift of the equilibrium in one direction or the other. One of the most informative means for identification of conformers in the DOP series with four-coordinated phosphorus is the method of dipole moments (DM) [4]; the success of this method in the present instance can be attributed to the high polarity of the bonds with the P atom. Using this method and PMR spectroscopy, we have investigated the following 2-dialkylamino-2-thiono- and 2-oxo-DOPs:

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*For communication 30, see [1].