MASS-SPECTROMETRIC INVESTIGATION OF ELECTRON-IMPACT-INDUCED IONIZATION OF CHLORINE DIOXIDE AND CHLORYL FLUORIDE MOLECULES

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UDC 543.51:541.124.7:546.134:546.162'13

Fisher [1] investigated the formation of positive ions (PI) during ionization of ClO_2 molecules by electron impact (EI). This author determined the ionization potential (IP) of ClO and ClO_2 molecules: IP(ClO) = 11.1 ± 0.1 eV; IP(ClO_2) = 10.7 ± 0.1 eV; the bond energy of the first oxygen atom in the ClO_2 molecule was found to be D_0(O−ClO) = 55 ± 2 kcal/mole. Negative ions (NI) in the mass spectrum of ClO_2 were not investigated. No one has previously investigated the ionization of ClO_2F molecules.

We have investigated the formation of PI and NI in the mass spectrum of ClO_2F, and NI in the mass spectrum of ClO_2, to obtain new data and refine existing data on the thermochemical characteristics of these molecules. Simultaneously, we measured the appearance potentials (AP) of PI in the mass spectrum of ClO_2. The kinetic energies (E_k) of most of the PI and NI were measured.

EXPERIMENTAL

The apparatus and measurement procedure were described in [2]. We obtained ClO_2 by heating at 60°C a wetted mixture of $KClO_3$ and $H_2C_2H_4 \cdot 2H_2O$; it was freed of CO_2 and kept in a glass capsule, located in a Dewar flask with dry ice.

The mass spectrum of PI, corresponding to the initial admission of ClO_2 into the mass spectrometer, contained mainly O^+, O_2^+, Cl^+, and Cl_2^+ ions; ClO_2^+ and ClO^+ ions were absent. It seems that the presence of oxygen and chlorine ions in the mass spectrum is due to decomposition of ClO_2 on the inner surface of the components of the mass spectrometer and admission system. We were able to greatly reduce the degree of decomposition of ClO_2 by prolonged heating of the admission system and analyzer tube at 300-400°C in the presence of argon, followed by direct heating of this oxide. The moment when the intensity of the Cl_2^+ ion peak (m/q = 70) was ~1% of that of the ClO_2^+ ion (m/q = 67) was taken as the end of passivation. During recording of the ionization efficiency curves (IEC) and the curves of the ion distribution with respect to E_k, the components of the ion source and the analyzer tube of the mass spectrometer were additionally cooled with liquid N_2.

As the source of ClO_2F ions we used its complex with BF_3 − tetrafluoroborate chloride $ClO_2^+BF_4^-$. The salt was kept in a quartz capsule at −78°C. The vapor pressure of ClO_2F and BF_3 above the salt at ~20 °C is 225 torr. The IR spectrum of the gas exhibits bands of ClO_2F and BF_3.

Like ClF_3 [3], ClO_2F actively reacts with the unpassivated surface of the components of the admission system and the mass spectrometer. As a consequence the mass spectrum of the PI is represented mainly by ClO_3F^+, ClO_3^+, SiF_3^+, Cl_2^+, ClO_2^+, ClO^+, HCl^+, Cl^+, O_2^+, HF^+, and F^+ ions. It is probable that besides halogenation of the surface of the components and of the substances adsorbed on it, we observe decomposition of ClO_2F; this is indicated by the high intensity of the O_2^+ ions. Simultaneously, the mass spectrum displays BF_3^+, BF_2^+, and BF^+ ions as a result of ionization of BF_3. To economize on ClO_2F, the surface was passivated with ClF_3 by the procedure in [3]. This measure was justified, because the molecular ion ClO_2F^+ was detected directly when we introduced a mixture of ClO_2F and BF_3 into the passivated mass spectrometer. The ClO_3F^+ and ClO_3^+ ions disappeared from the mass spectrum, and the intensities of the other accompanying ions were sharply reduced. It was found that at the moment of replacement of ClF_3 in the admission system by a mixture of ClO_2F and BF_3, the mass spectrum displayed ClF_3^+, ClF_2^+, and ClF^+ ions. When the gas in the admission system was replaced thrice, these ions disappeared altogether from the mass spectrum; this is attributable to adsorption of ClF_3 on the surface of the components of the admission system and the mass spectrometer at the moment of passivation, followed by its desorption when the gas was changed. The distinguishing

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Institute of New Chemical Problems, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1963-1971, September, 1980. Original article submitted October 16, 1979.

0568-5230/80/2909-1385$07.50

TABLE 1. Relative Intensities, Appearance Potentials (AP), and Kinetic Energies (E_k) of Positive and Negative Ions in the Mass Spectrum of ClO_2*

m/q	Ion	Data of Fisher [1]		Authors' data		
		relative intensity	AP, eV	relative intensity	AP, eV	E_k, eV
72	Cl_2^+	—		0,6		
70	Cl_2^+	—		1,0		
69	ClO_2^+	32,0		33,0		
67	ClO_2^+	100	10,7±0,1	100	10,77±0,10	0,032±0,004
53	ClO^+	10,1		16,0		
51	ClO^+	31,3	13,5±0,1	48,2	13,55±0,08	0,043±0,006
44	CO_2^+	10,4		14,2		
38	HCl^+	0,5		1,2		
37	Cl^+	0,6		3,2		
36	HCl^+	1,5		3,8		
35	Cl^+	1,9		9,5		
32	O_2^+	2,1		7,1		
28	N_2^+; CO^+	4,1		7,0		
53	ClO^-			32,5		
51	ClO^-			100	0,27±0,07	0,059±0,017
37	Cl^-			13,2		
35	Cl^-			40,6	0,23±0,07	—
32	O_2^-			1,1	0,00±0,03	0,020±0,020
16	O_I^-			—	≈1	—
16	O_{II}^-			1,1	3,75±0,07	

*The mass spectrum of PI corresponds to 70 V of ionizing potential. The NI current intensity was measured at the IEC maximum.

feature of the mass spectrum of a mixture of ClO_2F and BF_3 is a constant change in the Cl_2^+ ion current intensity. In the case of liquid N_2 cooling of the mass-spectrometer analyzer tube and the ion source components, at the beginning of admission of a mixture of ClO_2F and BF_3, the mass spectrum does not exhibit Cl_2^+ ions, but after 30 min the Cl_2^+ ion current intensity becomes sufficient to mask the $ClOF^+$ ion, coinciding in mass with the Cl_2^+ ion (m/q = 70 and 72). This means that we were unable to measure the AP of the $ClOF^+$ ion.

DISCUSSION OF RESULTS

Chlorine Dioxide. Table 1 gives the relative intensities, the AP, and the E_k of the ions in the mass spectrum of ClO_2. Figures 1-3 show the IEC, PI, and NI. Our data for the PI agree completely with those in [1]. Using photoelectron spectroscopy, Bulgin et al. [4] found that the first vertical IP of the ClO molecule is 11.01 ± 0.01 eV. The combination of this value of the IP(ClO) with our measured values of AP(ClO^+) and E_k of the ionization products in the process

$$ClO_2 + \vec{e} \rightarrow ClO^+ + O + 2\vec{e} \qquad (1)$$

gives, for the upper limit of the bond energy of the first oxygen atom in the ClO_2 molecule, the value D_0(O–ClO) = 2.40 ± 0.08 eV or 55.3 ± 1.9 kcal/mole. This value agrees with that given in a reference work [5] (57.6 ± 1.5 kcal/mole).

Fisher [1] noted distinguishing features in the IEC of the ClO_2^+ ion. We also observed complexities in the IEC of this ion, manifested in the absence of a linear sector of the curve from the AP up to 14.5 eV. Such behavior of the IEC cannot be attributed to the electron energy distribution. This phenomenon remains obscure.

In the mass spectrum of the NI the most intense ion ClO^- is formed from the ClO_2 molecule in the process

$$ClO_2 + \vec{e} \rightarrow ClO^- + O \qquad (2)$$

Calculation of the electron affinity (EA) of the ClO molecule, taking account of the measured AP(ClO^-) and E_k of the ionization products and the calculated value of D_0(O–ClO) = 2.40 ± 0.08 eV, gives the value EA(ClO) ≥ 2.35 ± 0.12 eV or 54.2 ± 2.8 kcal/mole. According to [5], D_0(O–ClO) = 2.91 eV. In [5] the estimated value of the heat of hydration of the ClO^- ion was used and therefore the result is an estimate.

During resonance capture of an electron by the ClO_3F molecule, Dibeler et al. [6] obtained three values for AP(ClO^-): 2.4 ± 0.3, 4.6 ± 0.3, and 8.5 ± 0.3 eV. In our opinion, the processes of formation of the ClO^- ion

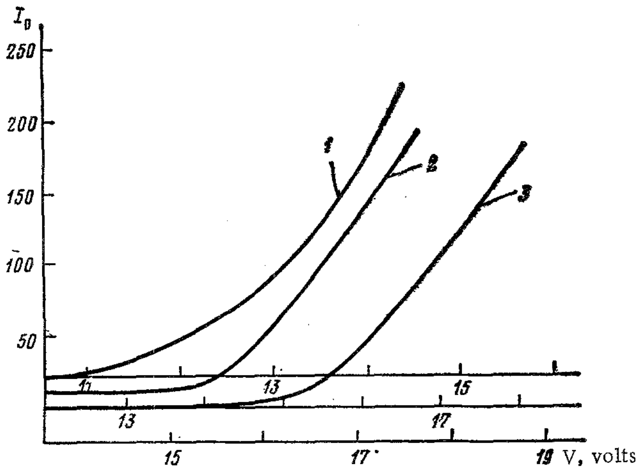

Fig. 1

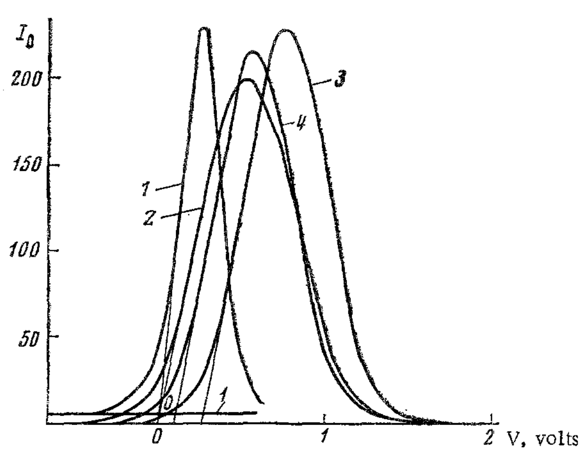

Fig. 2

Fig. 1. Ionization efficiency curves of ClO_2 with formation of positive ions: 1) ClO_2^+; 2) ClO^+; 3) Ar^+. Here and below the ion current is given in arbitrary units. The middle scale of abscissas refers to curve 2, the lower one to curve 3.

Fig. 2. Ionization efficiency curves of ClO_2 with formation of negative ions: 1) SF_6^-; 2) O_2^-; 3) ClO^-; 4) SF_5^-.

from the ClO_3F molecule, postulated in [6], are doubtful. The difference in the first two values of the AP of ClO^- agrees with the bond energy of the atoms in the OF molecule [5]; therefore, it is preferable to assign the first two potentials to the processes

$$ClO_3F + \vec{e} \rightarrow ClO^- + O + OF \qquad (3)$$

$$ClO_3F + \vec{e} \rightarrow ClO^- + 2O + F \qquad (4)$$

The third value of $AP(ClO^-)$ possibly corresponds to a process with a high value of the sum of the excitation energies and the E_k of the ionization products. Calculation of EA(ClO) from the equation of the energy balance corresponding to process (4), using the data of [5] and the value $\Delta Hf_{298}(ClO_3F) = -5.40 \pm 0.24$ kcal/mole [7], gives the value $EA(ClO) \geq 2.6 \pm 0.3$ eV. This value agrees with the one we obtained.

Like the ClO^- ion, the O_2^- ion of the ClO_2 molecule is uniquely formed by the scheme

$$ClO_2 + \vec{e} \rightarrow O_2^- + Cl \qquad (5)$$

Taking account of the thermochemical data in [5], the calculated $AP(O_2^-)$ in process (5) is -0.28 ± 0.07 eV. The existence of the O_2^- ion in the mass spectrum of ClO_2 indicates the presence of an excitation energy of the ionization products in process (5), equal to 0.24 ± 0.09 eV.

The IEC of the O^- ion exhibits two peaks. Owing to the low relative intensity of the first peak, the origin of the curve is estimated as 1 eV. Linear extrapolation (see Fig. 3) gives the value of 3.75 ± 0.08 eV for $AP(O^-)$. This value agrees closely with the calculated value 3.78 ± 0.06 eV, obtained by taking account of the thermochemical characteristics [5], if we assume that the O^- ion is formed in the process

$$ClO_2 + \vec{e} \rightarrow O^- + O + Cl \qquad (6)$$

Similar calculation of $AP(O^-)$ in the process

$$ClO_2 + \vec{e} \rightarrow O^- + ClO \qquad (7)$$

gives the value 1.02 ± 0.06 eV. Our estimated value of $AP(O^-)$, corresponding to the IEC origin, coincides with the calculated value. We can therefore assert that formation of the O^- ion in processes (6) and (7) is possible, but the probability of formation of this ion in (6) is higher.

Formation of the Cl^- ion from the ClO_2 molecule is also possible in the two processes

$$ClO_2 + \vec{e} \rightarrow Cl^- + O_2 \qquad (8)$$

$$ClO_2 + \vec{e} \rightarrow Cl^- + 2O \qquad (9)$$

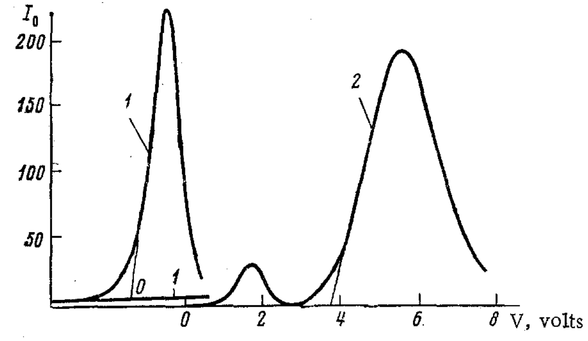

Fig. 3

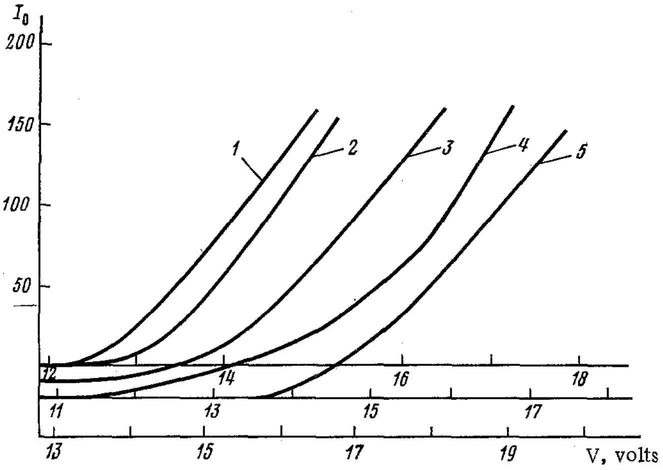

Fig. 4

Fig. 3. Ionization efficiency curves of ClO_2 with formation of negative ions: 1) SF_6^-; 2) O^-.

Fig. 4. Ionization efficiency curves of ClO_2F with formation of positive ions: 1) Xe^+; 2) ClO_2F^+; 3) ClO_2^+; 4) ClO^+; 5) Ar^+. The middle axis of abscissas refers to curve 3, the lower one to curves 4 and 5.

TABLE 2. Relative Intensities, Appearance Potentials, and Kinetic Energies of Positive Ions in the Mass Spectrum of ClO_2F

m/q	Ion	Relative intensity	AP, eV	E_k, eV
88	ClO_2F^+	1,5		
86	ClO_2F^+	4,4	12,41±0,10	0,021±0,004
74	Cl_2^+	<0,01		
72	Cl_2^+; $ClOF^+$	4,1		
70	Cl_2^+; $ClOF^+$	11,9		
69	ClO_2^+	33,0		
68	BF_3^+	6,0		
67	BF_3^+; ClO_2^+	100	11,1±0,3 13,15±0,08	0,015±0,006
53	ClO^+	4,2		
51	ClO^+	12,8	13,41±0,08 16,07±0,06	0,041±0,009
49	BF_2^+	32,8		
48	BF_2^+	7,3		
44	CO_2^+	3,6		
38	HCl^+	2,4		
37	Cl^+	0,4		
36	HCl^+	7,4		
35	Cl^+	1,4		
32	O_2^+	3,0	12,16±0,05	0,014±0,006
30	BF^+	0,06		
29	BF^+	0,01		
28	N_2^+; CO^+	0,6		

The AP(Cl^-) in these processes, calculated from thermochemical characteristics [5], are −3.48 ± 0.06 and 1.62 ± 0.06 eV, respectively. Comparison of the calculated values with AP(Cl^-) = 0.23 ± 0.07 eV excludes process (9) from the examination. Process (8) is possible when the sum of E_k and the excitation energy of the ionization products is 3.71 ± 0.09 eV. It is more probable that the Cl^- ion is formed during ionization of the molecules of some accompanying gaseous chloride.

Chloryl Fluoride. Tables 2 and 3 give the AP, E_k, and relative intensities of the PI and NI in the mass spectrum of ClO_2F. Table 2 includes the mass spectra of BF_3 and other accompanying gases. Figures 4 and 5 give the IEC of most of the recorded ions in the mass spectrum of ClO_2F.

Dudin et al. [8] showed that the systematic overestimate of the AP in the electron impact (EI) method in comparison with the photoionization method is less than 0.1 eV. In this connection the measured AP of the ClO_2F^+ ion corresponds to the upper limit of the adiabatic IP of the ClO_2F molecule and is 12.41 ± 0.10 eV.

The origin of the IEC of the ClO_2^+ ion corresponds to 11.1 ± 0.3 eV. The IEC has a break at 13.15 ± 0.08 eV. Within the limits of reproducibility of the results the first value coincides with IP(ClO_2) (see Table 1).

TABLE 3. Relative Intensities, Appearance Potentials, and Kinetic Energies of Negative Ions in the Mass Spectrum of ClO_2F

m/q	Ion	Relative intensity	AP, eV	E_k, eV
72	$ClOF^-$	10,8		
70	$ClOF^-$	32,1	0,88±0,12	0,050±0,010
69	ClO^-_{2I}	3,8		
	ClO^-_{2II}	6,2		
67	ClO^-_{2I}	11,6	0,66±0,09	0,040±0,005
	ClO^-_{2II}	18,5	3,50±0,11	0,043±0,012
56	ClF^-	10,4		
54	ClF^-	32,6		
53	ClO^-_{I}	4,8		
	ClO^-_{II}	32,3		
51	ClO^-_{I}	15,2	0,33±0,10	0,038±0,011
	ClO^-_{II}	100	3,53±0,10	0,061±0,010
37	Cl^-	10,0		
35	Cl^-	31,5		

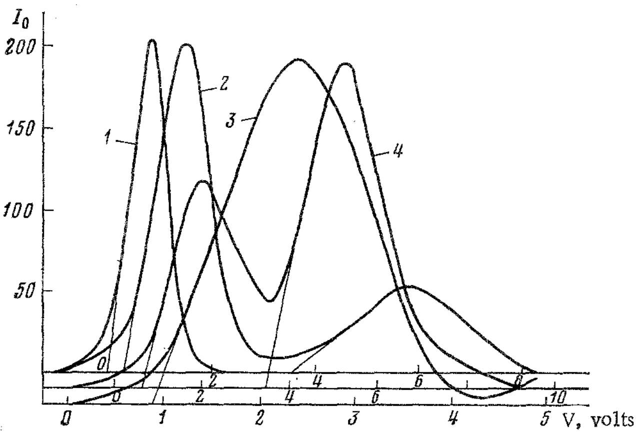

Fig. 5. Ionization efficiency curves of ClO_2F with formation of negative ions: 1) SF_6^-; 2) ClO^-; 3) $ClOF^-$; 4) ClO_2^-.

This may indicate that ClO_2F reacts with the surface of the components of the mass spectrometer, leading to formation of ClO_2. The break on the IEC is most likely due to formation of the ClO_2^+ ion in the process

$$ClO_2F + \vec{e} \rightarrow ClO_2^+ + F + 2\vec{e} \qquad (10)$$

and is manifested more strongly in the case of liquid N_2 cooling of the components of the ion source and mass-spectrometer analyzer chamber, owing to the decrease in the intensity of the initial sector of the IEC. This is further proof that the AP(ClO_2^+) of process (10) is 13.15 ± 0.08 eV. Taking account of the measured E_k of the ionization products of the ClO_2F and ClO_2 molecules, the difference in AP(ClO_2^+) and IP(ClO_2) gives for the bond energy of the fluorine atom in the ClO_2F molecule the value $D_0(F-ClO_2) = 2.38 \pm 0.13$ eV or 54.9 ± 3.0 kcal / mole.

From the viewpoints of structure and behavior in relation to cooling with liquid N_2, the IEC of the ClO^+ ion is analogous to that of the ClO_2^+ ion. Within the limits of the experimental error the origin of the IEC, corresponding to 13.41 ± 0.08 eV, coincides with the AP of the ClO^+ ion from the ClO_2 molecule (Table 1); this is additional proof of the presence of ClO_2 in the region of the ionization chamber. We assign the break on the IEC to the process

$$ClO_2F + \vec{e} \rightarrow ClO^+ + O + F + 2\vec{e} \qquad (11)$$

Taking account of the E_k of the ionization products in process (11), the difference in AP(ClO^+) = 16.07 ± 0.06 and IP(ClO) = 11.01 ± 0.01 eV [4] gives for the energy of detachment of fluorine and oxygen atoms the value $D_0(O, F-ClO) = 5.00 \pm 0.06$ eV or 115.3 ± 1.4 kcal/mole. In this case the bond energy of the first oxygen atom in ClO_2F is 2.62 ± 0.14 eV or 60.4 ± 3.2 kcal / mole. Taking account of [5], calculation of the $\Delta H^0_{f0}(ClO_2F)$ from processes (10) and (11) leads to the values −10.8 ± 3.4 and −13.4 ± 1.5 kcal/mole, respectively; the mean value is −12.1 ± 1.4 kcal/mole, agreeing with the value $\Delta H^0_{f298}(ClO_2F) = -8.1 \pm 12.5$ kcal/mole, obtained by the thermochemical method [9].

The IEC of the $ClOF^-$ ion exhibits another peak, corresponding to dissociative capture of an electron by the ClO_2F molecule with AP($ClOF^-$) = 0.88 ± 0.12 eV. The $ClOF^-$ ion can be formed from the ClO_2F molecule only by the scheme

$$ClO_2F + \vec{e} \rightarrow ClOF^- + O \qquad (12)$$

Bearing in mind the above-calculated value of the bond energy $D_0(ClOF-O)$ and the measured AP and E_k of the ionization products in process (12), we obtain EA(ClOF) = 2.00 ± 0.19 eV or 46.1 ± 4.4 kcal/mole. Furthermore, the values obtained above for $\Delta H^0_{f0}(ClO_2F)$ and $D_0(ClOF-O)$ permit calculation of the heat of formation of the ClOF molecule: $\Delta H^0_{f0}(ClOF) = -29.8 \pm 3.5$ kcal/mole. In the calculation we used the data of [5].

The IEC of the ClO_2^- ion displays two resonance peaks. Clearly, there are two ways in which the ClO_2^- ion can be formed from the ClO_2F molecule, the ionization products having different excited states. In that case we naturally assign the lower value AP(ClO_2^-) = 0.66 ± 0.09 eV to the ionization process

$$ClO_2F + \vec{e} \rightarrow ClO_2^- + F \qquad (13)$$

with the low value of the excitation energy of the ionization products. Calculation of the electron affinity from the measured AP and E_k of the ionization products in process (13), taking account of the above-calculated bond energy $D_0(F-ClO_2)$, gives the value $EA(ClO_2) \geq 1.77 \pm 0.16$ eV or 40.8 ± 3.7 kcal/mole. The literature does not give the exact value of the EA of the ClO_2 molecule. The value given in [5], 3.43 eV, is a distortion of the data of Weiss [10], who gives the value 2.8 eV. The value $EA(ClO_2) = 2.8$ eV, taken by the authors of [5] from [10], was erroneously attributed to the EI method. In the calculation of $EA(ClO_2)$, Weiss [10] used the estimated heat of hydration of the ClO_2^- ion. Without exact data on the heat of hydration of the ClO_2^- ion, we must regard the value of 2.8 eV for $EA(ClO_2)$ as an estimate. Zolotukhin et al. [11] measured the thermal effect of the reaction

$$ClO_{2\,soln} + \vec{e} \rightarrow ClO^-_{2\,soln} \tag{14}$$

$\Delta H_{298} = 25.71$ kcal/mole. However, owing to the absence of data on the heats of hydration of the ClO_2^- ion and the ClO_2 molecule we cannot use this value for calculating the electron affinity of ClO_2. For subsequent use, we recommend the value 1.80 ± 0.16 eV as the value of $EA(ClO_2)$.

The IEC of the ClO^- ion also exhibited two peaks corresponding to two processes of its formation. The AP and E_k of the ion, determined from the first peak, are practically the same as those of the ClO^- ion formed during resonance capture of an electron by the ClO_2 molecule. Above, for the case of the AP of ClO^+ and ClO_2^+ ions we showed that the ClO_2F investigated contained ClO_2 as an impurity. The coincidence of the $AP(ClO^-)$ here and for ClO_2 is also attributable to the presence of ClO_2 in the gas. In that case the second AP of the ClO^- ion, $AP(ClO^-) = 3.53 \pm 0.10$ eV, very probably belongs to the capture of an electron by the ClO_2F molecule. There are two possible routes of formation of the ClO^- ion from a ClO_2F molecule

$$ClO_2F + \vec{e} \rightarrow ClO^- + OF \tag{15}$$

$$ClO_2F + \vec{e} \rightarrow ClO^- + O + F \tag{16}$$

Calculation of the electron affinity of the ClO molecule by (15) and (16) gives the values $EA(ClO) = -0.69 \pm 0.25$ and 1.53 ± 0.14 eV, respectively. The first of the negative values indicates that there is no possibility of formation of the ClO^- ion from a ClO_2F molecule by Eq. (15). The second value has the meaning of the lower limit of the EA of the ClO molecule. Therefore, of the two above-calculated values of the electron affinity of the ClO molecule we recommend the value 2.35 ± 0.12 eV for subsequent use.

At present the measured value of $AP(Cl^-)$ in the mass spectrum of ClO_2F cannot be assigned to any particular process of formation of the Cl^- ion.

CONCLUSIONS

1. Using the electron-impact method the authors have investigated the ionization of ClO_2 and ClO_2F molecules with formation of positive and negative ions.

2. They have calculated the energies of the $F-ClO_2$, O, $F-ClO$, and $O-ClOF$ bonds, the heats of formation of ClO_2F and ClOF, and the lower limits of the electron affinity of ClO, ClO_2, and ClOF molecules.

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