

DRIFT Study of the Photolysis Products in Crystalline Perchlorates $MClO_4$ ($M = K, Rb, Cs$ and NH_4)

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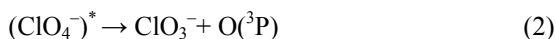
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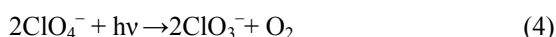
Abstract – The spectra of the $MClO_4$ ($M = K, Rb, Cs$ and NH_4) polycrystalline samples under photolysis ($\lambda_{ex}=185+254$ nm, 298K) were measured by the methods of Diffuse Reflectance Infrared Fourier Transform Spectroscopy. It was found that the ClO_3^- and ClO_2^- are the main products of $KClO_4$, $RbClO_4$ and $CsClO_4$ photolysis. Only ClO_3^- was found in photolysed NH_4ClO_4 . The obtained results are confirmed the photolysis model for the isostructural crystalline alkali perchlorates earlier proposed by authors of this article.

1. Introduction

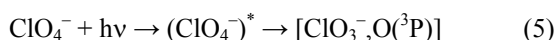
The earliest paper devoted to the perchlorate photolysis was published in 1980 [1]. It has been shown that the excitation of ClO_4^- in aqueous solutions by 184.9 nm light produces $O(^3P)$ with a quantum yield of unity and ClO_3^- . The quantum yield for O_2 formation averages slightly greater than one half (0.53). This result shows that most of the $O(^3P)$ atoms recombine and only a small fraction react with ClO_4^- in dilute solutions. The next reactions for the perchlorate photolysis were proposed



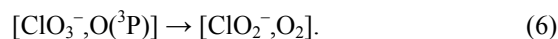
Later on O_2 and ClO_3^- have been established as primary products in the photolysis of solid $KClO_4$ at 185 nm and 77K, whereas Cl^- is the dominant product of secondary photolysis [2]. It is proposed that the primary photolytic process is photoionization, in which an electron is transferred between adjacent anions. The net process was proposed corresponding to the primary products ClO_3^- and O_2



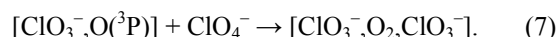
Recently, we have reported the results of the room temperature crystalline alkali perchlorates photolysis investigation by chemical analysis and ESR spectroscopy methods [3]. It has been suggested, that the primary photolytic process is the same that in aqueous perchlorate solution [1], namely reaction (1). But because of the "cage effect" the rupture of the Cl-O bond in a $MClO_4$ crystalline matrix leads to formation of the complex



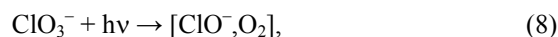
It is proposed that the future transformation of this intermediate product depend on the nature of the escaped $O(^3P)$ atom. One way of the reaction is the internal rearrangement



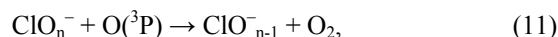
Another way is the external process as the chemical reaction



This secondary intermediate products of the reactions (6) and (7) are dissociate later to independent particles ClO_3^- , ClO_2^- and O_2 . These substances are known to absorb exciting lights of the used lamp so the next secondary photolytic processes are took place:



The triplet oxygen $O(^3P)$ formed in the matrix initiate further transformations of neighboring anions



there $n = 1, 2, 3$.

So a sequence of reactions (5–11) account for the formation of all photolytic products [3].

We could not find any publications about results of ammonia perchlorate photolysis investigation.

The goal of the present paper is to analyse the IR spectra of at room temperature photolysed alkali and ammonium perchlorates crystals to determine the photolysis products and their accumulation immediately in solid state.

2. Experimental

Polycrystalline samples were grown by slow cooling of saturated aqueous solutions. The perchlorates used were a.r. grade (twice crystallized from redistilled water before use).

IR reflection spectra of polycrystalline samples were recorded on a Bruker model "TENSOR 27" spectrometer with Diffuse Reflections Unit (A 528-P) "EasyDiff" in the range 450–4000 cm^{-1} (resolution less than 2 cm^{-1}) at room temperature. The spectra were analyzed using OPUS program.

The samples were irradiated at room temperature with a low-pressure mercury vapour lamp with quartz tube DRB-8, whose irradiation consist of mainly two lines 185 and 254 nm (intense ratio 1:10 approximately). Maximum photolysis times were equal to 3 hour. Spectra were recorded by cycle irradiation-registration with 15 minute step.

Elementary processes

Table I. Vibration frequencies (in cm^{-1}) of the observed lines for photolysed samples of MClO_4 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$ and NH_4) and their assignment to photolysis products

KClO_4	RbClO_4	CsClO_4	NH_4ClO_4	Assignment
489	487	483		$\nu_4(\text{ClO}_3^-)$
806	805	798		$\nu_1(\text{ClO}_2^-)$
848	847	842		$\nu_3(\text{ClO}_2^-)$
932	931	930	924	$\nu_1(\text{ClO}_3^-)$
968	966	965		$\nu_3(\text{ClO}_3^-)$
981	979	977	975	$\nu_3(\text{ClO}_3^-)$
991	990	987		$\nu_3(\text{ClO}_3^-)$
			2220, 2240	X
941,1	939,7	937,5	935,8	$\nu_1(\text{ClO}_4^-)$

Table II. Vibration wavenumbers (cm^{-1}) of the ClO_3^- impurity ion embedded in crystalline host matrix

Matrix	ν_1	ν_3	ν_4	$\nu_1+\nu_3$
KClO_4	932	969, 981, 992	489	1906, 1917, 1924
RbClO_4	931	967, 980, 991	487	1906
CsClO_4	935	966, 977, 987	483	
NH_4ClO_4	924	964, 981	486	
K_2SO_4	940	1007	488, 491	1900

3. Results

Fundamental bands both of the ClO_3^- and ClO_2^- are displayed in IR spectra of all samples exposed to the light of the above-mentioned lamp from 15 minutes to three hour exposition except for NH_4ClO_4 .

Only the ClO_3^- bands and another unknown product X bands at 2220 and 2240 cm^{-1} are displayed in the later case.

Visual effects and IR spectra data of the photolysed NH_4ClO_4 are not so clear in contrast to other perchlorates under investigation. The surfaces of NH_4ClO_4 crystals stand milk-white at appearance and opaque under photolysis.

Vibration frequencies of the observed lines for photolysed samples of MClO_4 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$ and NH_4) and their assignment to photolysis products are summarized in Table I. The assignment was done by analysis of common published results (for example, see the [4] tables).

As is known the IR diffuse reflectance spectra and IR absorption spectra sometimes may have significant differences in some details. Most of published in literature spectral information are given for IR absorption spectra. Therefore for the most reliable assignment of the experimentally obtained results we have grown the MClO_4 and K_2SO_4 crystals with embedded by cocrystallization from aqueous solution ClO_3^- impurity (the impurity content approximately a few molar %) and examined its IR diffuse reflectance spectra.

Vibration wavenumbers of the ClO_3^- impurity ions embedded in host crystals are summarized in Table II. As seen, the internal modes of the imbedded ion ClO_3^- agree closely with the bands of the photolysis products in photolysed MClO_4 matrixes.

The intensity of all bands of the ClO_3^- and ClO_2^- ions is increasing proportionally to the time of irradiation. The accumulation curves are presented in Fig. 1 and Fig. 2.

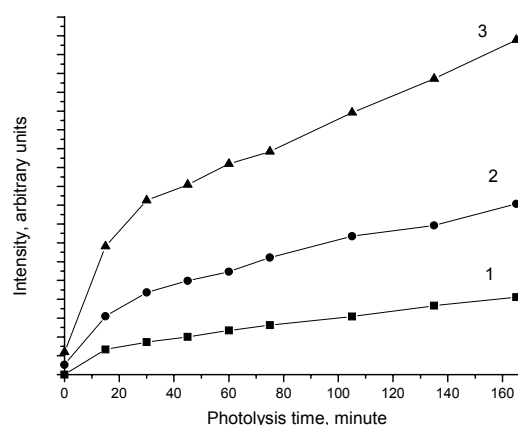


Fig. 1. The curves of ClO_3^- (980 cm^{-1} band) accumulation vs. photolysis times for alkali perchlorates (1 – KClO_4 , 2 – RbClO_4 , 3 – CsClO_4)

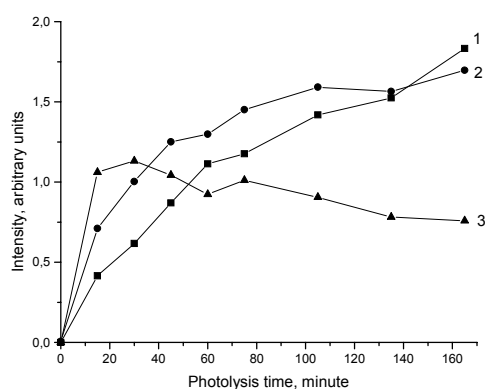


Fig. 2. The curves of ClO_2^- (848 cm^{-1} band) accumulation vs. photolysis times for alkali perchlorates (1 – KClO_4 , 2 – RbClO_4 , 3 – CsClO_4)

It should be mentioned that matrix bands of all substances under investigation trend to the intensities increase and linewidth shrinkage in all matrixes.

4. Discussion

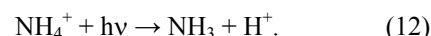
As seen from the data of Table I the frequencies of the observed bands of photolysis products in samples of MClO_4 ($M = \text{K, Rb, Cs}$ and NH_4) depends on the host matrix nature and unambiguously decrease in the following order $\text{KClO}_4 - \text{RbClO}_4 - \text{CsClO}_4 - \text{NH}_4\text{ClO}_4$. The frequencies of the all fundamental internal vibrations of host matrix anion ClO_4^- decreases in the same manner as well (see for example the values of $\nu_1(\text{ClO}_4^-)$ vibration mode in Table I). It is strongly suggested that the observed products are formed in the bulk of host matrix not on the surface of samples.

The accumulation curves of all the observed products have as minimum two distinguishable areas. The accumulation rates of ClO_3^- at initial photolysis times up to narrow 20 minutes are about twice faster in comparison with the same one at the second area (photolysis times from 40 minutes to maximum irradiation time 165 minute). The accumulation rate in the initial times mainly depends on from the rate of formation by reactions (5) and (7). And at the second area accumulation is formed by equilibrium of the mentioned formation reactions and secondary photolytic annealing reactions (8), (10) and (11).

The accumulation curves of ClO_2^- are formed by the same nature processes ClO_2^- but has unusual form since ClO_2^- has the absorption maximum at 250 nm which coincides well with the strongest intense line of lamp emission of 254 nm.

Current data are in good correlation with the results of the quantitative analysis of stable ionic product accumulation in photolysed alkali perchlorates [3].

Only two photolysis products have been detected in photolysed NH_4ClO_4 and these, ClO_3^- and X, are formed in small concentration in comparison with other perchlorates under investigation. X denotes the product with bands at 2220 and 2240 cm^{-1} and may be attributed to direct ammonium ion photolysis product because of their presence in the only photolysed NH_4ClO_4 and the absence in other perchlorate matrixes. One of the primary processes of the NH_4^+ photolysis may be the proton expulsion as well as the primary process for perchlorate (see reactions 1–2)



More work to study the detail of the ammonium ion photolysis under 185 nm excitation needs to be carried out.

The ClO_2^- band absence and the ClO_3^- presence in photolysed NH_4ClO_4 spectra may be attributed to the reaction (7) preference but not the internal rearrangement of $[\text{ClO}_3^-, \text{O}(\text{P})]$ complex.

One of the ways to explain the NH_4ClO_4 surface modification under photolysis is the active evolution of the gaseous photolysis products.

5. Conclusion

To conclude, let us summarize our principal findings.

The primary consequence of perchlorate photolysis is the breaking of chlorine–oxygen bond.

Our study demonstrates that earlier proposed sequence of reactions (5–11) really account for the photochemical processes in crystalline perchlorates isostructural with MClO_4 [3].

It's necessary to consider also the ammonium decay to account for the photochemical processes in crystalline NH_4ClO_4 and other ammonium containing salts.

References

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