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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Fisica. — *Positive and negative ion–molecule reactions in* SF_6 (*).

Nota di Anna Giardini–Guidoni, Roberto Tiribelli e Fernando Zocchi, presentata (**) dal Corrisp. G. Sartori.

Riassunto. — In uno spettrometro di massa da ricerca sono state studiate le reazioni di molecole di SF_6 con ioni negativi e positivi prodotti in CH_4, O_2, NH_3, CO_2 ed SF_6. Ad elevate concentrazioni di SF_6 in sorgente (2.10^{16} mol cm^{-3}) si osserva la stabilizzazione per collisione degli ioni SF_6^+ ed SF_6^- prodotti per ionizzazione β. Un analogo processo di stabilizzazione è osservato quando gli ioni SF_6^+ ed SF_6^- sono fatti collidere con Ar, CH_4, CO_2, O_2 ed NH_3. Si sono inoltre misurate le costanti di velocità per la reazione tra CH_5^+ ed SF_6 che conduce alla formazione di SF_5^+ ed HF e per la reazione di scambio di carica tra O_2^- ed SF_6.

Introduction.

The importance of electron scavenging processes in radiolysis was first recognized a long time ago [1], but only recently has the attention of radiation chemists been redirected towards these processes as a results of the discovery of their influence on product yields [2].

Among electron scavengers sulphur hexafluoride has been extensively used [3] because of its high electron capture cross section [4] and its relatively high electron affinity [5]. However, in many studies specific electron capture has been assumed without having information about the complicating effects caused by reactions with species other than electron. To obtain direct evidence of the interaction of SF_6 molecules with the positive and negative ionic species formed in some irradiated systems, we have studied the ion molecule reactions which take place, when SF_6 is added to these systems in the β–ray ion source of a high pressure mass spectrometer [6].

Experimental.

This work was carried out with the double inlet research mass spectrometer already described [6]. The procedure employed for data collection was the same as in previous studies [7]. The positive ionic reactions were investigated operating the β–ray ion source with the repeller field fixed at 2 V/cm and with the ion accelerating voltage set at 1000 V. The apparatus was adapted to the study of negative ionic reactions by reversing the electric

(*) Work supported by C.N.R.
(**) Nella seduta del 15 novembre 1969.

and magnetic fields in the ion source and tube analyzer. The negative ions, after mass analysis, were collected on an electron multiplier connected to an amplifier. The output was sent to both a counting system and a linear ratemeter and then recorded.

For the study of mixtures the β–ray ion source was operated by fixing the pressure of one component and measuring the intensities of the ions formed. Then the second component was added through the second inlet and the mass spectrum was recorded as a function of its variable partial pressure.

The concentration of each compound in the ion source was usually varied between 5×10^{-3} and 0.6 torr.

Commercially available sulphur hexafluoride (stated purity 98 %) was purified by bulb to bulb distillation. Extra high purity A_r, O_2, CH_4, CO_2 and NH_3 were used without any further purification.

RESULTS AND DISCUSSION.

a) *Positive ions.*

Pure SF_6. In Table I the relative intensities of the positive ions produced by β–ionization in pure SF_6 are reported as a function of SF_6 concentration in the ion source. At relatively low pressure (5×10^{-2} torr) the observed mass spectrum is qualitatively in agreement with that observed with 70 eV electrons [8], the only discrepancy being the presence of a less intense peak at mass 108 (SF_4^+). This fact can be explained as due either to the absence of pyrolysis effects on the β–ray source or to a lower level of impurity in our gas.

TABLE I.

Positive ions formed in SF_6 (% *of total ions*) *as a function of the* SF_6 *pressure in the ion source.*

$p_{FS_6}^{ion}$ Torr	S^+	SF^+	SF_2^+	SF_3^+	SF_4^+	SF_5^+	SF_6^+
0.0001 (*) . . .	3.5	5.5	3.6	17.2	5.6	62.5	—
0.05	4.5	5.5	4.5	17.0	—	69	0.3
0.1	2.7	5.9	4.6	17.0	—	69	1.1
0.2	2.2	4.2	5.0	17.0	0.5	70.5	1.3
0.3	2.15	4.5	5.7	18	0.8	70	1.2
0.4	2.1	4.0	6.0	17	2.1	67.5	3.2
0.5	2.1	4.3	6.2	16.2	3.7	57	4.05

(*) Data taken from reference [7].

At higher pressures SF_6^+ ions were observed; at the highest pressure studied (0.5 torr), they account for about 4 % of the total positive ionic current. The formation of the molecular ion SF_6^+ has been observed previously at low pressure in a photoionization experiment [9], but with an intensity several orders of magnitude lower than that of SF_5^+.

Therefore it has been suggested [9] that SF_6^+, formed in an excited state, in a very short time dissociates into $SF_5^+ + F$. The pressure dependence observed in our experiments is in agreement with this hypothesis and indicates that a process of deactivation by collision is operative at higher pressures:

$$(1)\qquad (SF_6^+) \longrightarrow SF_5^+ + F$$

$$(2)\qquad (SF_6^+) \xrightarrow{+M} SF_6^+$$

If it is assumed that the stabilization is due to a typical ion molecule interaction, and therefore the rate constant of process (2) is of the order of 10^{-1} cm^3 mol^{-1} sec^{-1}, it is possible to estimate the mean life time of the excited SF_6^+ to be of the order of 10^{-6} sec [12].

Reactions of methane ions with SF_6.

At a pressure of CH_4 in the ion source of 0.6 torr the ions CH_5^+, $C_2H_4^+$, $C_2H_5^+$, $C_3H_5^+$ and $C_3H_7^+$ account for about 99 % of the total ionic current [13]. The reactions of these ions with SF_6 molecules were studied by adding a variable pressure of SF_6 in the ion source. In fig. 1 the results of these expe-

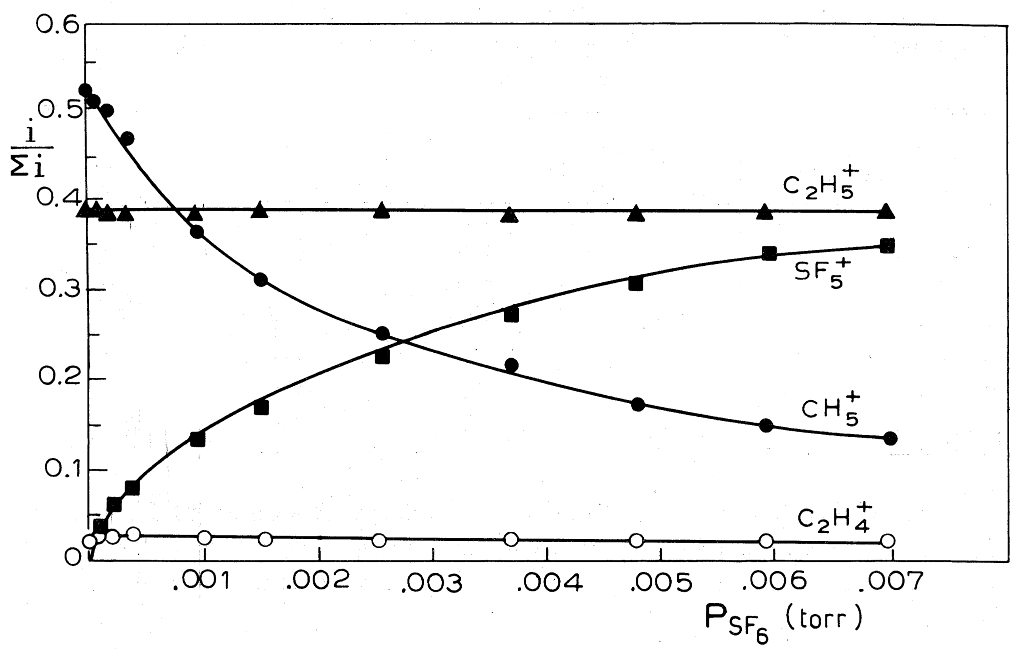

Fig. 1. – Relative intensity of the ions formed as a function of SF_6 partial pressure when the pressure of CH_4 is 0.6 torr in the ion source.

riments are reported. It can be seen from the figure that only CH_5^+ ions appear to react with appreciable rate ($K \simeq 3 \times 10^{-10}$ cm^{+3} mol^{-1} sec^{-1}) with SF_6 to produce SF_5^+ ions. The only process which can reasonably explain the formation of this ion is that leading to CH_4 and HF as neutral products:

$$CH_5^+ + SF_6 \rightarrow SF_5^+ + CH_4 + HF \tag{3}$$

in spite of the fact that this reaction is slightly endothermic on the basis of the presently known heat of formation of SF_5^+ [9, 14].

b) *Negative ions.*

The β–ray negative spectrum of pure SF_6 is quite simple. As can be seen from Table II, only SF_6^- and SF_5^- ions are detected at the lowest pressure investigated (6×10^{-4} torr) and their ratio is about 11.5. At higher pressure this ratio increases and other ions are observed: F^-, a metastable ion around m/e 110 and an ion at m/e 165; however their relative intensities do not exceed a few percent of the total even at the highest pressure investigated (0.6 torr). The ion at m/e = 165 which can be identified as the complex ion, SF_7^- accounts, at 0.6 torr, for 0.3 % of the total yield, indicating that consecutive ionic processes occur only to a negligible extent in pure sulphur hexafluoride. It has been established previously [10, 17] that negative ions in SF_6 are formed by a resonant capture process and that the electron is first attached to form metastable ions which then decompose in several different ways.

TABLE II.

Negative ions formed in SF_6 (% *of total ions*) *as a function of the* SF_6 *pressure in the ion source.*

$P^{ion}_{SF_6}$ Torr	F^-	SF_5^-	SF_6^-	SF_7^-
0.0006	—	8.0	92.0	—
0.075	—	7,0	93	—
0.15	0.3	3.9	95.5	0.1
0.2	0.3	3.5	96.0	0.2
0.35	0.5	3.3	96.0	0.2
0.45	1.0	2.7	96.0	0.3

The triangles in fig. 2 indicate that the decay of excited SF_6^- ions into SF_5^- can be prevented if the pressure is high enough for collisional deactivation to be operative as indicated in the following scheme:

$$e + SF_6 \longrightarrow SF_6^- \longrightarrow SF_5^- + F \tag{4}$$

$$SF_6^- \xrightarrow{+M} SF_6^- \tag{5}$$

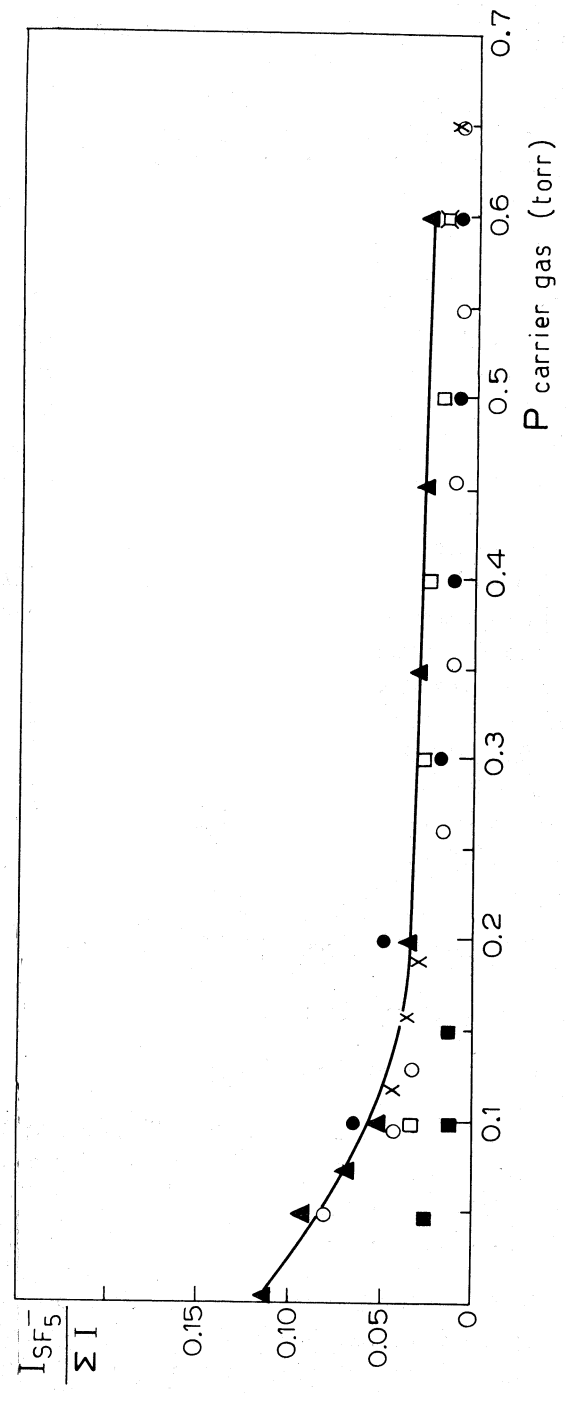

Fig. 2. – Yield of SF_5^- ions as a function of carrier gas pressure at field strength E = 2 V/cm when the partial pressure of SF_6 is 6×10^{-4} torr in the ion source ▲ SF_6, ■ NH_3, o CH_4, □ O_2, ● Ar, × CO_2. The curve is the best fit of experimental points for SF_6.

The same arguments used above for positive ions allow us to establish that the life time of the state decaying into SF_5^- is of the order of 10^{-6} sec.

Analogous behaviour is observed when SF_6 is added in small quantities to some other gases i.e. CH_4, O_2, Ar, NH_3 and CO_2. The data reported in fig. 2 show that when a partial pressure (6×10^{-4} torr) of SF_6 is established in the ion source, any increase in the concentration of one of the above compounds causes a lowering of the ratio SF_5^-/SF_6^-. The total negative ion current increases almost linearly as a function of pressure up to more than 15 times the initial value (fig. 3).

This increase can be explained with a careful examination of the processes occurring in the ion source. In fact when a gas of high ionization cross section (carrier gas) is admitted in the source a great number of low energy secondary electrons are formed [11]. These secondary electrons, in a cascade process, produce positive ions and nearly thermal electrons, which in turn are captured by SF_6 molecules [4, 10] with high efficiency. Thus, it may be explained why a pressure increase enhances the total yield of SF_6 negative ions even though charge exchange processes between the negative ions of the carrier gas and SF_6 occur only to a low extent.

The reactions of negative ions formed in O_2, CO_2 and NH_3 with SF_6 molecules were also investigated. In these experiments the partial pressure of the carrier gas was kept constant in the ion source while that of the SF_6 molecules was varied between 3×10^{-4} and 5×10^{-3} torr.

At a pressure of 0.5 torr of O_2 in the ion source the relative intensities of the negative ions formed: O^-, O_2^- and O_3^- are respectively 80 %, 15 % and 5 % [13]. Of these ions only the O_2^- appear to react with SF_6 molecules, and from the decrease of the absolute intensity of O_2^- (Table III) a value of 2×10^{-10} $cm^3\,mol^{-1}\,sec^{-1}$ is calculated [6] for the constant of the reaction:

$$O_2^- + SF_6 \rightarrow O_2 + SF_6^- \tag{6}$$

while the rate constant for the reaction:

$$O^- + SF_6 \rightarrow O + SF_6^- \tag{7}$$

is found to be lower than 10^{-12} $cm^3\,mol^{-1}\,sec^{-1}$. The fact that reaction (7) does not take place would suggest that the electron affinity of SF_6 is lower than 33.7 Kcal/mole [14]. From reaction (9) the upper limit is found to be 27.3 Kcal/mole [14, 15] about 7 Kcal/mole lower than the previous estimate [5].

The intensity of CO_3^- ions present at a pressure of 1 torr of CO_2 in the ion source does not decrease when SF_6 is added at various pressures, indicating that the rate constant of the following reaction (8) is lower than 10^{-12} $cm^3\,mol^{-1}\,sec^{-1}$:

$$CO_3^- + SF_6 \rightarrow CO + O_2 + SF_6^- . \tag{8}$$

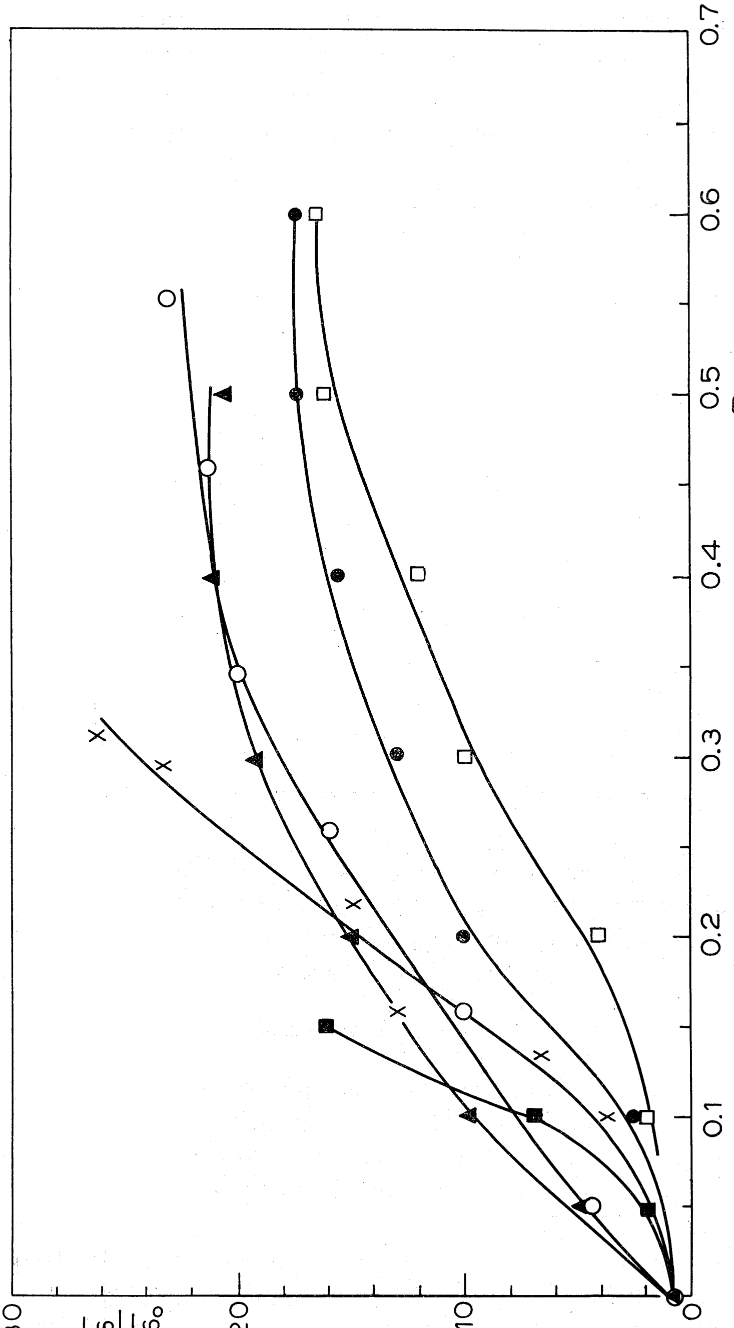

Fig. 3. – Increase in the yield of SF_6^- ions as a function of carrier gas pressure at field strength E = 2 V/cm when the partial pressure of SF_6 is 6×10^{-4} torr in the ion source ▲ SF_6, ■ NH_3, ○ CH_4, □ O_2, ● Ar, × CO_2.

TABLE III.

Decrease in the absolute intensity of O_2^- *ions as function of* SF_6 *partial pressure in the ion source.*

V Rep. 2.4 V – Partial pressure of $O_2 = 0.5$ Torr.

P_{SF_6} Torr	$O_2^-/O_2^-{}_0$
0	1.00
$3 \cdot 10^{-3}$	0.88
$6 \cdot 10^{-3}$	0.83
$9 \cdot 10^{-3}$	0.795
$1.2 \cdot 10^{-2}$	0.735
$1.5 \cdot 10^{-2}$	0.715
$1.8 \cdot 10^{-2}$	0.675
$2.1 \cdot 10^{-2}$	0.63
$2.4 \cdot 10^{-2}$	0.57
$3.0 \cdot 10^{-2}$	0.455
$3.6 \cdot 10^{-2}$	0.39
$4.35 \cdot 10^{-2}$	0.325

The NH_2^- ions, which at a pressure of 0.15 torr account for 99.9 % of the total negative ionic current (the only other ions being the $N_2H_5^-$), do not appear to react with SF_6 molecules and a lower limit of 10^{-12} cm^3 mol^{-1} sec^{-1} can be set for the rate constant of the reaction:

$$NH_2^- + SF_6 \rightarrow NH_2 + SF_6^- . \qquad (9)$$

The results reported above indicate that the use of SF_6 as electron scavenger can produce secondary effects which cannot be underestimated. The addition of SF_6 in methane radiolysis can noticeably decrease the yield of CH_5^+ because of process (3) and consequently the yield of H atoms coming from neutralization of CH_5^+.

As far as the negative ionic reactions are concerned, the high rate constant of reaction (6) confirms that the addition of SF_6 to CO_2 has the effect of removing the oxidizing O_2^- ions produced, during the irradiation of CO_2 and consequently, increases the initial yields of O_2 and CO [15].

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