THE INFLUENCE OF SOME HEXAFLUOROMANGANATES(IV) ON THE REACTION BETWEEN XENON AND FLUORINE UNDER PRESSURE*

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The influence of potassium, silver, nickel and xenon hexafluoromanganates(IV) on the reaction between xenon and fluorine was investigated. The reaction was followed in a static system. A xenon to fluorine mole ratio 1 : 4.5 was used and the total pressure of the gaseous mixture amounted to 36 atm as measured at 22° C; the reaction temperature was 120° C. Among the listed hexafluoromanganates(IV) the catalytic influence of silver and nickel hexafluoromanganates(IV) was found to be the greatest. In the presence of these complexes the formation of xenon difluoride is a heterogeneous reaction and of first order with respect to xenon.

INTRODUCTION

Studying the influence of manganese trifluoride on the reaction rate of xenon-fluorine at 120° C, it was found that a part of the xenon present reacts with the manganese compound and that this new formed compound — xenon hexafluoromanganate(IV) — catalyses the xenon-fluorine reaction (1,2). To elucidate the behaviour of this compound on the xenon-fluorine reaction, the influence of potassium, silver and nickel hexafluoromanganates(IV) was studied. The influence of these complexes was followed at a pressure amounting 36 atm as measured at 20° C while the reaction temperature was 120° C. In order to compare the activities of complex and binary fluorides, the influence of silver and nickel difluorides was also investigated. The specific reaction rates in the presence of the mentioned hexafluoromanganates(IV) are given here.

EXPERIMENTAL

Materials

Fluorine was produced and purified in this laboratory as described elsewhere (3,4). Xenon was supplied by L'Air Liquide (Paris, France) in 99.5 per cent purity.

Potassium hexafluoromanganate(IV) was prepared by the action of bromine trifluoride on an equimolecular mixture of potassium permanganate and chloride [5]. The silver complex was synthetised by static fluorination of silver permanganate under pressure at 350° C [6]. Nickel hexafluoromanganate(IV) was obtained by the $MnCl_2$-$NiCO_3$ reaction in the melt of hydrazinium(2+)fluoride. The original compound was then fluorinated in a stream of elemental fluorine at 350° C [7]. The xenon complex was prepared by the reaction of MnF_2 with an excess of XeF_2 at 120° C [8].

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For the preparation of silver difluoride the fluorination of silver(I) oxide with elemental fluorine under pressure was introduced. Nickel difluoride was supplied by Koch-Light (Colnbrook, England). Chemical compositions and specific surface areas (BET — adsorption of N_2 at the liquid nitrogen temperature) of the listed compounds are given in Table 1.

Table 1

Chemical compositions and specific surface areas of hexafluoromanganates(IV) and difluorides

Compound	Calcd. composition (%)	Found. composition (%)	Specific surface area (m²/g) (BET)
$XeMnF_6$	Xe: 43.74, Mn: 18.29, F: 37.97	Xe: —, Mn: 16.8, F: 35.1	1.5
K_2MnF_6	K: 31.65, Mn: 22.22, F: 46.13	K: —, Mn: 22.2, F: 46.5	1.5
$NiMnF_6$	Ni: 25.79, Mn: 24.13, F: 50.07	Ni: 26.4, Mn: 24.5, F: 49.5	2.3
$AgMnF_6$	Ag: 38.97, Mn: 19.85, F: 41.18	Ag: 38.1, Mn: 18.6, F: 38.7	2.3
AgF_2	Ag: 73.95, F: 26.05	Ag: 73.9, F: 25.4	1.4
NiF_2*	Ni: 60.60, F: 39.40	Ni: 60.3, F: 39.0	10.4

Apparatus

The reaction between xenon and fluorine was followed in a 100 ml reaction vessel made of nickel. Pressure transmitters with nickel bellows in conjunction with oil-filled Bourdon gauges (160 mm dia. face, 0—60 atm, VDO-OTA, Frankfurt/Main, W. Germany, accuracy ±0.3 atm) were used for the measurements of pressure. The reaction vessel was immersed completely in a liquid bath. The gauges, complete with their pressure transmitters, were calibrated by the absolute method and the corrected pressure values were used in the estimation of pressure differences. Reaction vessels were heated by a thermostatted glycerine bath. A monel, 10 cm path length gas absorption cell fitted with silver windows and a Zeiss UR-20 spectrometer were used to obtained I. R. spectra of reaction products.

Procedure

The reaction vessel with catalyst was evacuated thoroughly and 30 atm of fluorine were metered into the vessel. The amount of fluorine was checked by weight and determined to ±1 mg. Xenon was condensed into the vessel by cooling with liquid nitrogen. The amount was also checked by weight (±1 mg). A xenon to fluorine mole ratio of 1 : 4.5 was always used. The total pressure of gas components was then checked at room temperature. The reaction vessel was immersed afterwards in the thermostatted bath which was kept at 120° C (±1° C). After the reaction had stopped the vessel was taken out and quenched at the liquid nitrogen temperature. The volatiles were separately pumped off at liquid nitrogen temperature, at −80° C and ultimately, at room temperature. The reaction products evolved at room temperature were monitored by I. R. spectroscopy.

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* Koch-Light, Cornbrook, England, after 24 hours fluorination (30 atm F_2) at 120°C

RESULTS AND DISCUSSION

The course of the reaction between xenon and fluorine as observed in the presence of 20 milimoles of xenon hexafluoromanganate(IV) is shown on Fig. 1. Hence it appears that the activity of $XeMnF_6$ obtained from manganese trifluoride in the system of xenon-fluorine at 120°C (1,2) is much greater than the $XeMnF_6$ prepared from manganese difluoride and xenon difluoride. This fact was also confirmed by following the reaction course in the presence of fluorinated (30 atm, 120°C) and unfluorinated $XeMnF_6$. The difference in activity may be caused by the greater specific surface area of $XeMnF_6$ prepared from manganese trifluoride. Fig. 2 shows the comparison of the reaction rates observed in the presence of equal amounts (20 milimoles) of the listed hexafluoromanganates(IV). The reaction stopped in the presence of all hexafluoromanganates(IV) when xenon difluoride was formed, except for the silver compound. The I. R. spectrum of products showed the presence of XeF_2 and XeF_4. According to the mass balance the yield on XeF_2 was higher than 80 per cent. In the presence of silver hexafluoromanganate(IV), however, xenon hexafluoride was found by I. R. spectroscopy to be partly formed in spite of the fact that the reaction was stopped at the point where only xenon difluoride should be formed.

The reaction between xenon and fluorine in the presence of the listed hexafluoromanganates(IV) is of first order with respect to xenon (zero order with respect to fluorine [9]). This is true, however, only in the first fourth of the time interval in which the pressure decreases and corresponds to the formation of XeF_2. This was confirmed by a straight line when plotted $\ln P_{Xe}$ versus time. Specific reaction rates as obtained from the slopes of $\ln P_{Xe}$ *vs.* time at 120°C and the activities — specific reaction rate per unit surface area — are shown in Table 2.

Xenon-fluorine reaction rate curves in the presence of equal amounts of AgF_2 and $AgMnF_6$, NiF_2 and $NiMnF_6$ are shown on Fig. 3 and Fig. 4, respectively. In the presence of silver and nickel difluorides more xenon tetrafluoride is formed in the reaction.

Table 2

Specific reaction rates of formation of XeF_2 in the presence of some hexafluoromanganates(IV) and difluorides at 120°C and their activities

Compound	Specific reaction rate, $k \cdot 10^5$ (sek^{-1})	Activity, $(k/S^*) \cdot 10^6$ (sek^{-1} m^{-2})
$NiMnF_6$	1.21	1.74
$AgMnF_6$	1.07	1.29
K_2MnF_6	0.31	0.43
$XeMnF_6$	0.39	0.42
NiF_2	2.40	1.19
AgF_2	2.01	5.46

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* S = total contact surface area

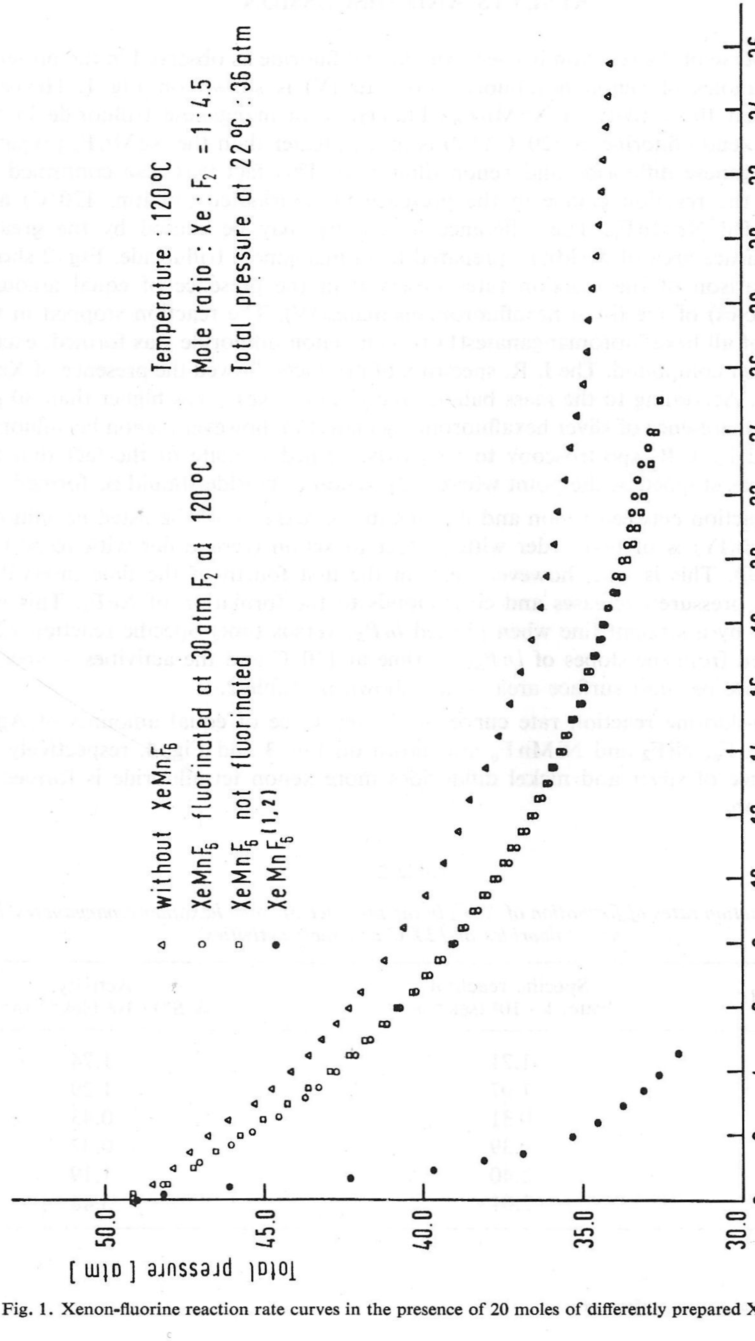

Fig. 1. Xenon-fluorine reaction rate curves in the presence of 20 moles of differently prepared $XeMnF_6$.

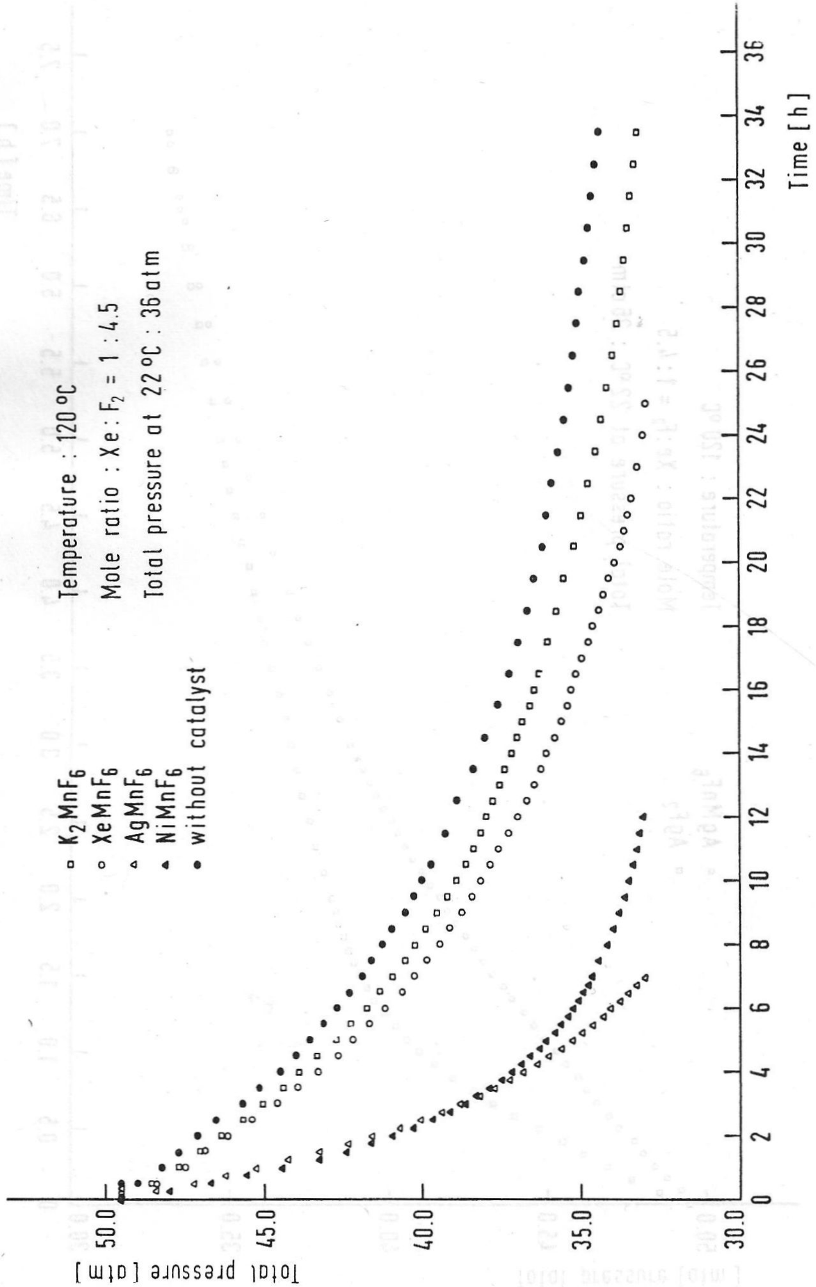

Fig. 2. Influence of 20 moles of $AgMnF_6$, $NiMnF_6$, $XeMnF_6$ and K_2MnF_6 on the rate of the xenon-fluorine reaction.

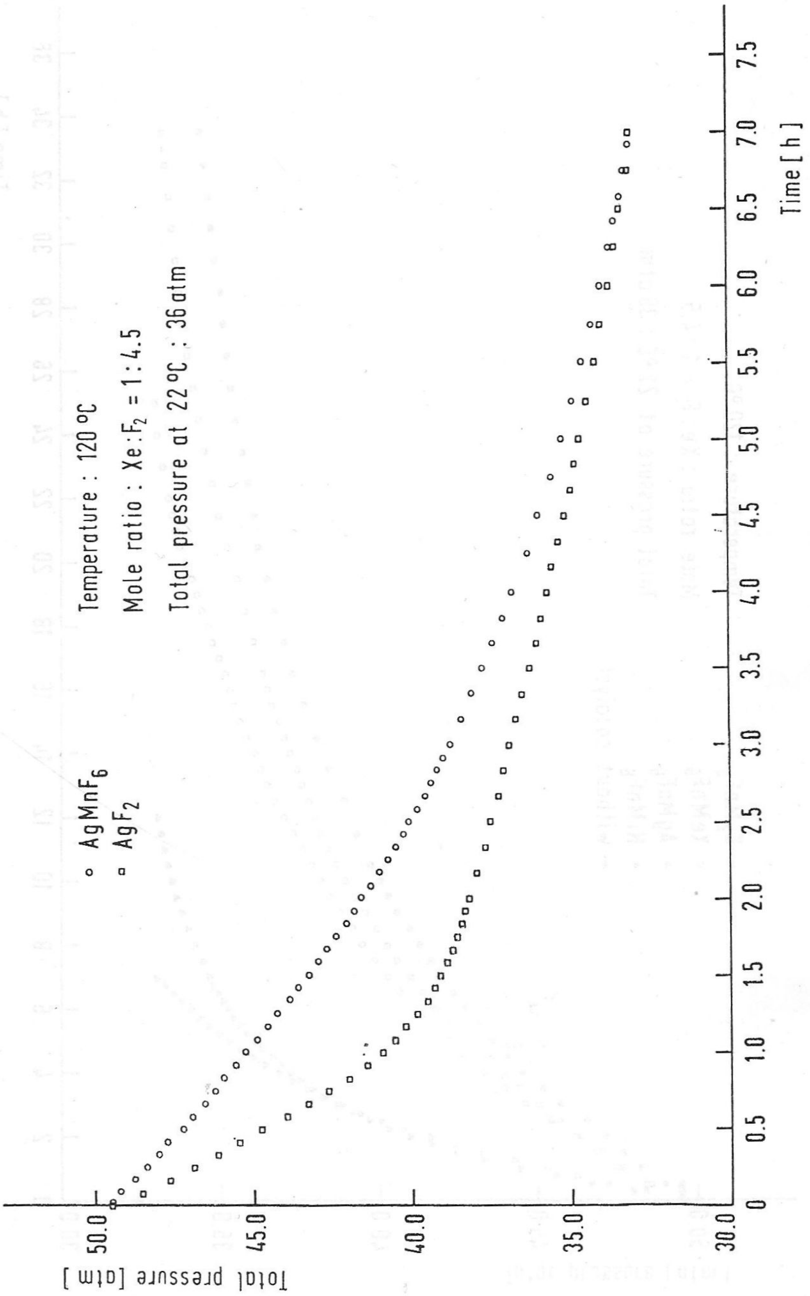

Fig. 3. Influence of 20 moles of AgMnF$_6$ and AgF$_2$ on the rate of the xenon-fluorine reaction.

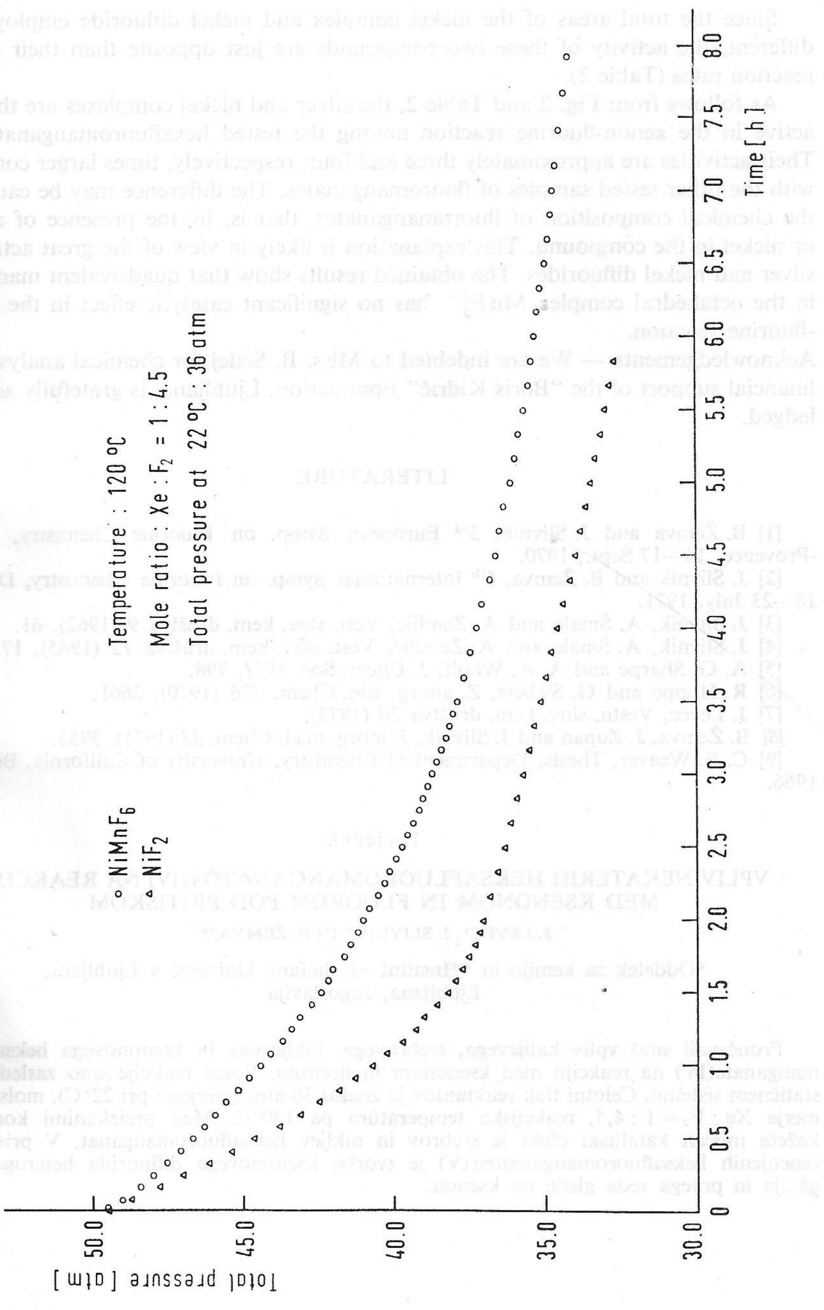

Fig. 4. Influence of 20 moles of $NiMnF_6$ and NiF_2 on the rate of the xenon-fluorine reaction.

Since the total areas of the nickel complex and nickel difluoride employed are different, the activity of these two compounds are just opposite than their specific reaction rates (Table 2).

As follows from Fig. 2 and Table 2, the silver and nickel complexes are the most active in the xenon-fluorine reaction among the tested hexafluoromanganates(IV). Their activities are approximately three and four, respectively, times larger compared with the other tested samples of fluoromanganates. The difference may be caused by the chemical composition of fluoromanganates, that is, by the presence of a silver or nickel in the compound. This explanation is likely in view of the great activity of silver and nickel difluorides. The obtained results show that quadrivalent manganese in the octahedral complex MnF_6^{2-} has no significant catalytic effect in the xenon-fluorine reaction.

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Izvleček

VPLIV NEKATERIH HEKSAFLUOROMANGANATOV(IV) NA REAKCIJO MED KSENONOM IN FLUOROM POD PRITISKOM

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Proučevali smo vpliv kalijevega, srebrovega, nikljevega in ksenonovega heksafluoromanganata(IV) na reakcijo med ksenonom in fluorom. Potek reakcije smo zasledovali v statičnem sistemu. Celotni tlak reaktantov je znašal 36 atm (merjeno pri 22°C), molsko razmerje $Xe : F_2 = 1 : 4,5$, reakcijska temperatura pa 120°C. Med preizkanimi kompleksi kažeta močan katalitski efekt le srebrov in nikljev heksafluoromanganat. V prisotnosti omenjenih heksafluoromanganatov(IV) je tvorba ksenonovega difluorida heterogena reakcija in prvega reda glede na ksenon.