EXTRACTION OF HAFNIUM. XIV.*
NITROPHENOLS AS SYNERGIC AGENTS

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The synergic effect of nitrophenols on the extraction of hafnium with N-benzoyl-N-phenylhydroxylamine (HA) from 2M-$HClO_4$ into benzene and nitrobenzene was studied. In benzene, the synergic effect increases in the order *o*-nitrophenol < dinitrophenols ≪ picric acid; in nitrobenzene, the effectiveness is reversed (2,6-dinitrophenol > picric acid). With benzene extraction the presence of one molecule of picric acid in the synergic complex was found. On the basis of slope analysis, the most probable extraction mechanism seems to be formation of the molecular complex HfA_4.HPi, in which the molecule of picric acid is hydrogen bonded to one of the nitrogen atoms of the co-ordinated ligand A^- in the HfA_4 chelate.

In the previous communication[1], synergic effects in the extraction of hafnium with N-benzoyl-N-phenyl-hydroxylamine (HA) in the presence of monobasic phenols and naphthols was studied. It has been shown that the synergic action of phenols is caused by their addition to the basic centres of the chelate HfA_4 through hydrogen bonding by the phenol hydroxyl. This mechanism was supported by, among other things, the fact that *o*-nitrophenol, whose hydroxyl group is blocked by intramolecular hydrogen bonding exhibited no synergic effect.

Since it could be assumed that nitrophenols with weaker intramolecular hydrogen bonding could act as synergic reagents, the extraction of hafnium using HA in the presence of dinitrophenols and picric acid was studied in this work.

EXPERIMENTAL

The preparation of the stock solution of the $^{175+181}Hf$ tracer in perchloric acid, the extraction technique, measurement of radioactivity and spectroscopic measurements have already been described[1-3]. The distribution ratio of hafnium (D) is given as the ratio of the γ-activities of $^{175+181}Hf$ in aliquots of the organic and the aqueous phases, as measured in a NaI (Tl) scintillation crystal. Before extraction, the aqueous phase contained the $^{175+181}Hf$ tracer in an overall concentration of $\leqq 7{\cdot}6 \cdot 10^{-6}$M in 2M-$HClO_4$; the organic phase contained HA and the synergic reagent. 2,4- and 2,5-dinitrophenol and picric acid were products of Lachema, 2,6-dinitrophenol was from the firm Loba-Chemie, Vienna. The solvents and perchloric acid used were of p.a. purity. The partition of picric acid and dinitrophenols between 2M-$HClO_4$ and

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benzene or nitrobenzene was measured photometrically on the photocolorimeter Pulfrich-Elpho. The measurements were carried out in the equilibrium aqueous phase at 415 nm.

RESULTS AND DISCUSSION

Extraction into Benzene in the Presence of Dinitrophenols

Figure 1 shows the dependence of the distribution ratio of hafnium on the concentration of dinitrophenols (DNP) and *o*-nitrophenol (*o*-NTP). The curve for *o*-NTP is taken from the work[1]. The pK_a values of the synergic reagents used are: *o*-NTP 7·2 (ref.[4]), 2,5-DNF 5·21 (ref.[5]), 2,4-DNP 4·08 (ref.[6]), and 2,6-DNF 3·69 (ref.[6]). In agreement with these values and with the suggested synergistic mechanism, dinitrophenols are better synergic agents than *o*-NTP. Among the dinitrophenols themselves, however, the correlation between synergic effect and acidity is not too satisfactory. Even though the strength of the intramolecular hydrogen bond decreases in the order 2,5- > 2,4- > 2,6-DNP, the first two agents exhibit practically identical synergic effects and, compared to them, 2,6-DNP at total 0·1M concentration exhibits only half as strong an effect. The partition of the dinitrophenols between 2M-$HClO_4$ and benzene has no effect on this order; 2,4- and 2,6-DNP are only negligibly transferred into 2M-$HClO_4$, with 2,5-DNP the partition is measurable (with an initial concentration of 0·1M, the equilibrium concentration in benzene after extraction is $9{\cdot}8 \cdot 10^{-2}$M), however the decrease in *D* following from it is within experimental error. With 2,6-DNF it is possible that the lower synergic effect is caused by the steric effect of the second nitro-group.

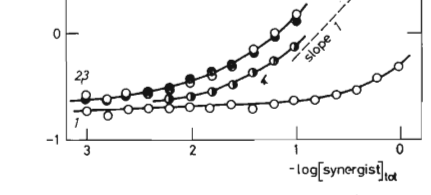

FIG. 1

The Dependence of *D* on the Concentration of *o*-NTP and DNP in Benzene $2 \cdot 10^{-3}$M-HA. Curve *1* *o*-NTP, *2* 2,6-DNP, *3* 2,5-DNP, *4* 2,4-DNP.

Fig. 2 shows the dependence of D on the overall concentration of HA for benzene and 0·1M solutions of dinitrophenols. The slope of 2·7 for pure benzene[1] is maintained in the presence of 0·1M 2,4- and 2,5-dinitrophenols; the presence of 0·1M-2,6-DNP leads to a decrease to 2·45. In contrast to phenol[1], no increase in the slope occurs here in the presence of a synergic agent. Because the overall synergic effect of dinitrophenols is small, it was not studied in further detail.

Extraction into Benzene and Toluene in the Presence of Picric Acid

In agreement with its much weaker intramolecular hydrogen bonding (pK_a, 0·71 ref.[7]) HPi is a much better synergic agent than the dinitrophenols. The dependences of log D on log $[HPi]_{tot}$ for extraction into benzene and toluene are given in figure 3. The upper limit of the curves is given by the solubility of HPi. In the range of $1 . 10^{-3}$

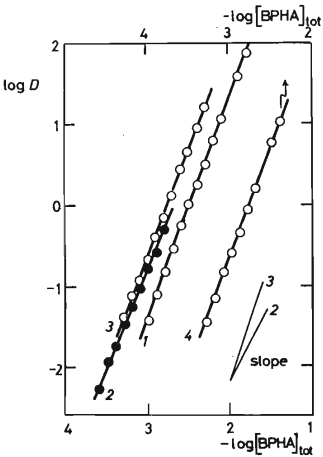

FIG. 2

The Dependence of D on the Overall Concentration of HA in Benzene

Curve *1* without synergic reagent, *2* 0·1M-2,6-DNP, *3* 0·1M-2,5-DNP, *4* 0·1M-2,4-DNP.

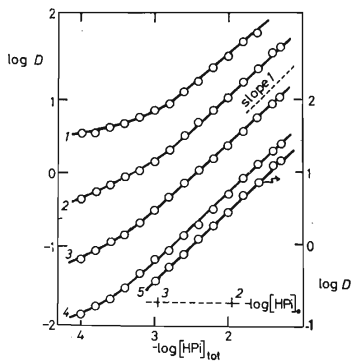

FIG. 3

The Dependence of D on the Overall or Equilibrium Organic Concentration of Picric Acid

Curves *1*—*4*: $4 . 10^{-3}$, $2 . 10^{-3}$, $1 . 10^{-3}$ and $5 . 10^{-4}$M-HA in benzene, *5* $2 . 10^{-3}$M-HA in toluene.

to $5 . 10^{-2}$M-HPi the plots are linear with a slope of +1. This is a considerable difference from the synergic effect of phenol[1], where the curves have a nonintegral slope of 1·5–2·0. This is probably caused by the fact that, in contrast to phenol, HPi is monomeric in benzene[8] and toluene[9] and the corresponding equilibria in a two phase system are considerably simpler. Because the shape of the plots is maintained even in $\log D - \log [\mathrm{HPi}]_{\mathrm{org,equil}}$ co-ordinates, where the correction for the partition of HPi between 2M-$HClO_4$ and benzene is introduced, the slope of +1 can be interpreted as the participation of one molecule of HPi in the reaction leading to formation of the synergic complex.

The $\log D - \log [\mathrm{HA}]_{\mathrm{tot}}$ plots for various constant concentrations of HPi in benzene and toluene are given in Figs 4 and 5. They have the form of pA curves. For $[\mathrm{HPi}] \ll$ $\ll$ 0·01M, their linear part in the region of low HA concentrations has the same slope as in benzene alone; with increasing HA concentration, the slope decreases to 2·0. With higher concentrations of HPi (0·025, 0·05M) the initial slope is lower (2·4–2·5)

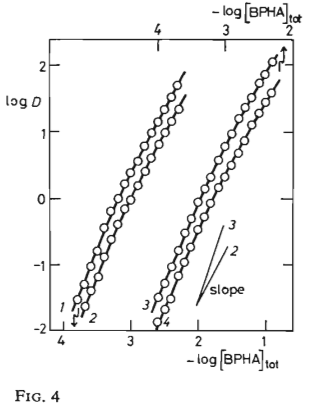

FIG. 4

The Dependence of D on the Overall Concentration of HA in the Presence of Picrjc Acid

Curve *1* 0·01M-HPi in benzene, *2* 0·01M-HPi in toluene, *3* 0·025M-HPi in benzene, *4* 0·025M-HPi in toluene.

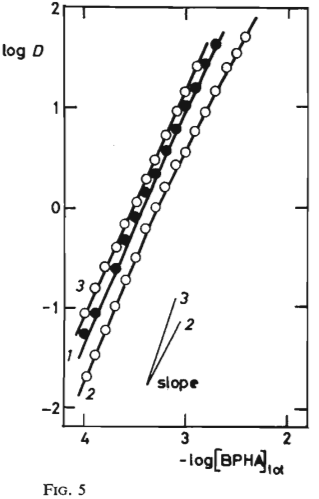

FIG. 5

The Dependence of D on the Overall Concentration of HA in the Presence of Picric Acid

Curve *1* 0·05M-HPi in benzene, *2* 0·05M-HPi in toluene, *3* 0·1M-HPi in benzene.

and the further shape of the curves is the same. The decrease of the slope from 2·6–2·8 to 2·4–2·5 with low HA concentrations is small, but well reproducible. For 0·1M-HPi, the slope decreases further to 2·2. It is clear that, as with dinitrophenols, the system with [HPi] behaves from this point of view in the opposite way to the system with phenol[1] where a gradual increase in the slope occurs with increasing concentration of phenol. This showed[1] that the original structure of the HfA_4 chelate was retained in the synergic complex. Considering the opposite trend of the log D *vs* log [HA] plots with [HPi] it is not possible to explain so unambiguously the synergic mechanism in the system Hf(IV)–HA–HPi. The synergism is, however, very marked even at $[HPi]_{tot} < 0{\cdot}01$M, where the slopes of these dependences are still the same as with benzene alone. For this reason we consider the most probable synergistic mechanism to be the addition of one molecule of HPi by hydrogen bonding to the tertiary nitrogen of the A^- ligand in the hafnium chelate. The same mechanism can be assumed with dinitrophenols. If the synergism were caused by substitu-

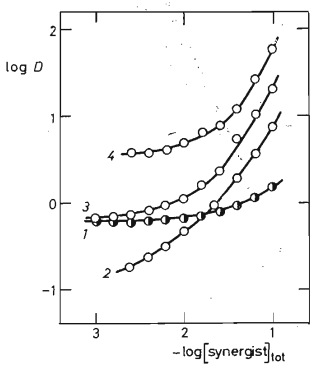

FIG. 6

The Dependence of D on the Concentration of Synergic Agents in Nitrobenzene

Curve *1* HPi, $4 \cdot 10^{-4}$M-HA, *2*–*4*: 2,6-DNP + $2 \cdot 10^{-4}$, $4 \cdot 10^{-4}$ and $8 \cdot 10^{-4}$M HA.

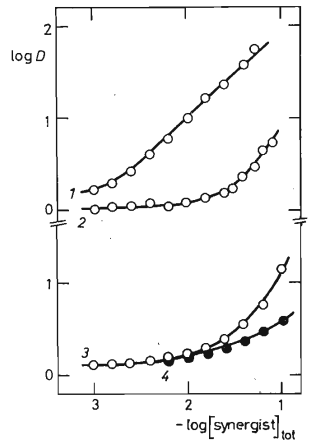

FIG. 7

The Dependence of D on the Concentration of Synergic Agents

Curve *1* HPi in *o*-dichlorobenzene, *2* 2,6-DNF in *o*-dichlorobenzene, *3* 2,6-DNF in benzonitrile, *4* HPi in benzonitrile.

tion of the co-ordinated ligand A^- for one picrate anion giving HfA_3Pi marked changes in the slope of the log D – log $[HA]_{tot}$ dependence would have to occur at an almost unchanged concentration of A^- in the aqueous phase.

The increase in the slope of these dependences in the system with phenol[1] was caused by the interaction of phenol with HA in the organic phase. Thus the course of the dependences in Figs 4 and 5 would indicate that an analogous interaction for HPi is much weaker. In fact the NMR spectrum of HA in $CDCl_3$ exhibits no shift of the signal of the hydroxyl proton of HA in the presence of HPi, and similarly the infrared spectrum of a mixture of HA and HPi in nujol in the OH absorption region represents only a superposition of the corresponding spectra of both components. Possible shifts of the carbonyl absorption of HA at 1620 cm^{-1} could not be followed because of the interfering effect of the absorption of HPi in this region. The most probable cause of the slight decrease in the slope of the log D – – log $[HA]_{tot}$ dependence can be assumed to be the lowering of the HA distribution ratio in the presence of picric acid due to which the concentration of A^- anion and the degree of complexation of the Hf^{4+} ion in the aqueous phase increase.

Extraction into Nitrobenzene

Figure 6 shows the synergic effect of 2,6-DNP and HPi with extraction into nitrobenzene solutions of HA. (Phenol, *o*-NTP, 2,4- and 2,5-DNP do not cause synergism in nitrobenzene). The order of synergic effectiveness of 2,6-DNP and HPi is the reverse to that for benzene and 2,6-DNP becomes a very effective synergic agent. The decrease in the synergic effectiveness of HPi is not typical of nitrobenzene alone. It occurs also in polar benzonitrile ($\varepsilon = 25{\cdot}2$, (ref.[10]) Fig. 7, curves *3*, *4*) while in *o*-dichlorobenzene ($\varepsilon = 9{\cdot}9$ (ref.[11]), curves *1* and *2*) this order is the same as in benzene.

The decrease in the synergic effectiveness of HPi is not caused by partition of HPi since, similarly as in neutral solutions[12], the distribution ratio of HPi in 2M-$HClO_4$ is larger for nitrobenzene than for benzene ($q_{HPi} = 31{\cdot}2$ for nitrobenzene/2M-$HClO_4$ and 7·5 for benzene/2M-$HClO_4$). Considering the equilibrium concentration of the synergic agent in the organic phase, nitrobenzene should be a more effective solvent. In fact the opposite is true and this is probably caused by the interaction of HPi with nitrobenzene. Spectroscopic measurements[13,14] show that the nitro group forms well defined, although weak, hydrogen bonds with proton donors and this interaction is also indirectly confirmed by acid-base[15] and extraction[12] studies. The product of this interaction is probably the molecular complex[15] HPi.NTB, for which the association constant[16] of 0·56 l/mol in chloroform has been determined (the analogous molecular complex of HPi with benzene has an association constant[16] of only 0·08 l/mol). Even though the association constant of the HPi.NTB complex is very low, the large excess of nitrobenzene in the synergic system leads to a marked decrease in the activity of HPi in the organic phase.

The curves for 2,6-DNP in nitrobenzene (Fig. 6) are reminiscent, in their shape and continually increasing slope, of the analogous dependences in the phenol synergic system[1]. The number of molecules of 2,6-DNP in the synergic complex cannot be unambiguously determined from the slopes. With reference to the above mentioned interaction of HPi with nitrobenzene and also to the fact that 2,4- and 2,5-DNP in nitrobenzene do not lead to any synergism, the reason for the marked synergic effect of 2,6-DNF in nitrobenzene remains unclear.

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