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A study of the mechanism of the reaction of $(C_2H_5O)_2AlC_2H_5$ with XeF_2 by ^1H and ^{19}F CIDNP

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Abstract

The integral chemically induced dynamic polarization (CIDNP) and multiple CIDNP have been found in the ^{19}F and ^1H NMR, respectively of the poorly studied oxidation of diethoxyethyl aluminium (I) with xenon difluoride (II) in toluene solution. This fact confirmed the radical mechanism proposed previously. The negative polarization of fluorine nuclei in the reaction products, such as ethyl fluoride (III) and fluorine toluene (IV), as well as the formation of ethyl radicals suggest that the appearance integral fluorine nuclei polarization in a heminal singlet pair of ethyl radical and $X\dot{e}F$ radical formed in the first stage of the reaction together with a basic product - diethoxyfluorine aluminium (V), is probably due to a single electron transfer. Multiple proton polarization in products III, ethyltoluene (VI) and butane occurs in diffusive impacts of ethyl radicals. The results from analyses of CIDNP effects enable us to propose a radical scheme of production of all products that are detected during the reaction: III, IV, V, VI, butane, ethane, ethylene, dibenzyl, ditolyl, and diethyltoluene.

Introduction

Up to now the mechanisms of oxidations of organometallic compounds by xenon difluoride have been studied in insufficient detail [1,2]. The analysis of the product content of the exothermal reaction of the organoaluminium compound $(C_2H_5O)_2AlC_2H_5$, with XeF_2 in toluene and the inhibition by galvinoxile, indicates a free radical mechanism for the reaction [3]. However, chemical nuclear polarization (CIDNP) is the most informative technique for studying radical reaction mechanisms [4]. CIDNP has also been used to determine in detail the reaction mechanisms of elementoorganic compounds [5]. ^{1}H and ^{19}F CIDNP has been used have to elucidate reaction mechanism of $(C_2H_5O)_2AlC_2H_5$ with xenon difluoride in toluene-d_8 and acetonitrile-d_3.

Experimental

Diethoxyethylaluminium (DEEA) was prepared by a previously described procedure [6]. The deuterated analogue DEEA-d_{10} was made similarly except that ethanol-d_6 was used.

Xenon difluoride was synthesized either photochemically [7] or under a high voltage [8] with further multiple sublimations in vacuo. Product purity was determined by iodomethric titration and by chromatography [9].

Deuterated solvents (Isotop) were used without further purification. Reactions were carried out with stirring under argon in solutions of DEEA or XeF_2 in the detector of the NMR spectrometer at room temperature. The ^{1}H and ^{19}F NMR spectra, were recorded on a JNM FX-90Q (JEOL) spectrometer.

Results

^{19}F NMR spectra. The spectrum of the initial XeF_2 shows two signals (Fig. 2a): a singlet with a shift of -182 ppm, and a doublet caused by spin–spin interaction with the ^{129}Xe nucleus. The reaction in acetonitrile shows a negative, polarized multiplet signal (-215 ppm) and a visible splitting of about 25 Hz, which we ascribe to CH_3CH_2F from literature data (Table 1). When the reaction is carried out in deuterotoluene, three further emission signals are observed at low field (Fig. 2b), and were assigned to the F atoms in the *o*-, *m*-, and *p*-positions of tolyl fluoride (Table 1). A multiplet structure of those signals is not encountered because at the moment of mixing the basic reaction product $(C_2H_5O)_2AlF$ separates out and gaseous Xe is released, which gives rise to an expansion of the NMR spectrum,

Table 1

Chemical shifts of ^{19}F NMR (CCl_3F), electron nuclear spin coupling parameters (Hz) of reaction products and CIDNP signs observed

Compound	δ (ppm) [a]	δ (ppm)	CIDNP signs
XeF_2	–	-182.8	no
		$J(^{129}Xe{-}F)$ 5600 Hz	
CH_3CH_2F	-215.8	-215.8	E
	$J H^1{-}F)$ 47.5 Hz	47	
	$J(H^2{-}F)$ 25.7 Hz	25	
$F\text{-}C_6H_4CH_3$	*o*- -120.5	-119.8	E
	m- -121.4	-123.3	E
	n- -126.0	-124.3	E

[a] Published data.

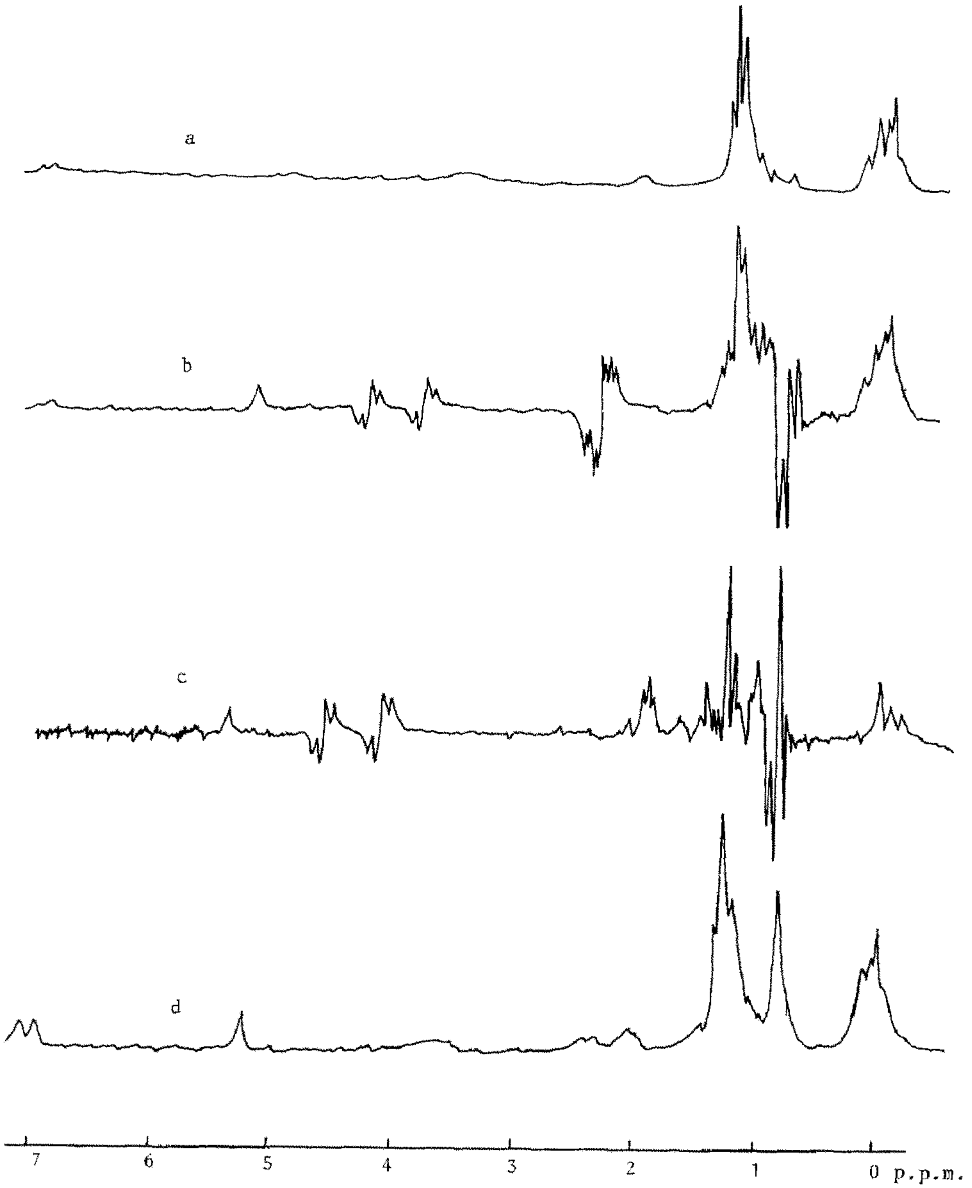


Fig. 1. ^{1}H NMR spectra (100 MHz) recorded during the reaction of $(C_2D_5O)_2AlC_2H_5$ (0.2 ml; 0.3 *M*) and with XeF_2 (0.2 ml, 0.10 *M*) solutions. a) Spectrum of initial AOC in toluene-d_8; b) 4 s after mixing of reagents in toluene-d_8; c) after 4 s in CD_3CN; d) products after 10 min in toluene-d_8.

which in turn masks the splittings caused by the small spin–spin interactions. The polarized fluorine-containing products are produced in very small amounts and were not detected in the final spectrum.

^{1}H NMR spectra. H CIDNP effects were studied with the use of DEEA and its deuterate analogue DEEA-d_{10} in acetonitrile-d_3 and in toluene-d_8. Fig. 1 shows the spectra obtained. As Figs. 1b, c show exclusively multiplet polarization is observed in the spectrum. At low field two polarized quartets are observed with E/A phase having a splitting of 47.6 Hz between them, which from the published data (δ 4.4 ppm and $J(^{19}F-^1H)$ 47.5 Hz) [10] were assigned to the methylene protons of ethyl

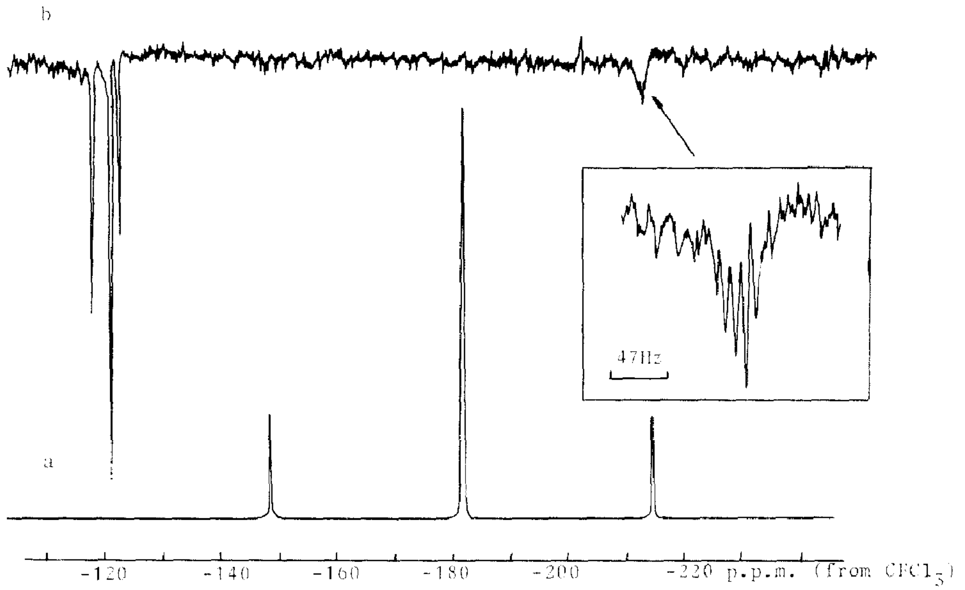


Fig. 2. ^{19}F NMR spectra recorded during the reaction of $(C_2H_5O)_2AlC_2H_5$ with XeF_2 in toluene solution. a) Initial XeF_2; b) 3–4 s after mixing of solutions.

fluoride. This signal is momentary, in analogy to that in the ^{19}F NMR spectra. When the reaction is carried out in toluene-d_8 (Fig. 2b), two polarized quartets are observed in the 2.4 ppm region, which were assigned to the methylene protons of *o*-, *m*-, and *p*-ethyltoluenes. The differences in the chemical shifts of the quartets was caused by that of the methylene proton occurring in various positions in respect to methyl group of toluene. Signals from the methyl protons of the ethyl fragments of

Table 2

Product yields, ^{1}H NMR chemical shifts and CIDNP signs for the reaction of DEEA with XeF_2 in toluene-d_8

Compound	Yield mol/mol XeF_2	Group	δ(ppm)	CIDNP signs
DEEA	2.0	CH_3	1.11; t	
		CH_2	0.1; k	
		CH_3	1.26; t	
		CH_2	3.74; m	
XeF_2	1.0			
$(C_2H_5O)AlF$	1.94			
Xe	0.97			
C_2H_6	0.9		0.82; c	no
C_2H_4	0.1		5.25; c	no
o-,*m*-,*p*-ethyltoluene	0.42	CH_2	2.43; k	E/A
dibenzene, ditolyl	0.15			
diethyltoluene	0.025			
tolyl fluoride	traces			
CH_3CH_2F	traces	CH_2	4.08	E/A
C_4H_{10}	traces		0.75–0.92	A/E

ethyltoluene and ethyl fluoride are obscured by the strong signals from the unchanged DEEA. The nonpolarized signals of ethylene and ethane are also observed during the reaction. The polarized lines at high field were assigned to butane, but, part of its field coincides with signals from unchanged DEEA, so its polarization has not been analyzed in detail.

The composition of the products, their NMR data, and CIDNP effects observed are listed in Table 2.

The addition of styrole, an effective radical trap which does not react with initial DEEA to the reaction mixture, suppresses all CIDNP effects.

Discussion

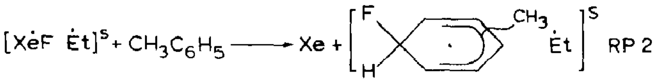
By modern concepts, integral polarization under high magnetic fields occurs only in radical pairs (RP), in which the radicals have differing g factors. The primary RP includes ethyl radical, as polarization is observed on ethyl fluoride. Its partner is most probably the $X\dot{e}F$ radical ($g = 2.075$), which occurs together with that of ethyl in the initial stages of the reaction by single electron transfer from DEEA to XeF_2:

$$XeF_2 + alEt \rightarrow alF + \left[X\dot{e}\ \dot{E}t\right]^S (RP1) \tag{1}$$

The unstable organoxenonic compound EtXeF probably results from the recombination of a primary *RP*1; further disproportionation gives a polarized EtF.

By the rules for CIDNP sign determination [11], a negative polarization on a product of intracell recombination may be observed only when the electron nuclear spin coupling on fluorine in the $X\dot{e}F$ radical is positive.

The coincidence of the ^{19}F CIDNP signs on ethyl fluoride and tolyl fluoride indicates that a tolyl fluoride is also the product of RP1 transformation. In the interaction of RP1 with a solvent cell, a secondary RP2 should come into existence with a multiplicity relating to RP1:



A spin density of the fluorine-substituted cyclohexadienyl radical formed is concentrated mainly at the *o*- and *p*-positions compared to fluorine substituted methylene group. A spin density grows on the fluorine nucleus by superconjugation, so electron nuclear spin coupling at the fluorine nucleus is positive and rather large (8.06 mT for the hexafluorinecyclohexadienyl radical) [2]. As a result the fluorine nucleus gains additional negative polarization for the products of intracell disproportionation:

$$RP2 \rightarrow FC_6H_4CH_3 + C_2H_4 \tag{3}$$

The yield of ethyl fluoride and tolyl fluoride is extremely small owing to the low probability of RP1 heminal recombination. Positive polarization of fluorine nuclei, therefore, may be observed in a radical that originates from the RP1. Nevertheless no signals with a positive polarization in ^{19}F NMR spectra are observed. We think that this is because of the rapid reaction of the XeF radical and DEEA:

$$X\dot{e}F + alEt \rightarrow alF + Xe + \bar{E}t \tag{4}$$

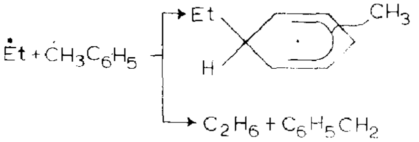
The alF compound precipitates and thus positive polarization of fluorine nuclei is not observed in the NMR spectrum.

Note that in the ^1H effect analysis only multiplet polarization is observed. Owing to the large difference, ΔgHO, for the RP1 (under the magnetic field strengths used) of 148 mT, the CIDNP in this pair will be found mainly on fluorine nuclei, in which A_F is 44.4 mT in the $\mathrm{X\dot{e}F}$ radical. The polarization on the protons in the ethyl radical is weak because of the large difference between A_H (A_{CH_2} 2.24 mT, A_{CH_3} 2.7 mT) and ΔgHO in the RP1. To confirm the observations, we have estimated the polarization that occurs in a heminal recombination pair $[\mathrm{X\dot{e}F}\ \dot{\mathrm{E}}\mathrm{t}]$ having the magnetic resonance parameters listed above. The calculation was carried out in $S - T_0$ limits of approximation for multinuclei RP by a programme compiled with ratios taken from ref. 13. The calculation shows that in the realistic choice of the RP kinetic parameters the integral polarization of fluorine nuclei is two orders greater than that of the equilibrium, whereas proton polarization of the ethyl group is at the same level of the equilibrium. The absence of integral polarization in the ^1H NMR spectrum because of heminal processes is accounted for by this fact. An estimation of the integral polarization for the RP2 provides a similar conclusion.

As was mentioned above, the addition of styrol to the mixture completely suppressed the CIDNP effects in the proton spectrum, which shows conclusively that proton polarization takes place in diffuse RP.

The dissociation of primary RP and its subsequent reaction (4) produces a large amount of ethyl radicals. Further transformations of ethyl radicals can be carried out as follows: the formation of diffuse RP with uncorrelated spins (5); a reaction with toluene to form a radical by "adhesion" (6) or the abstraction of hydrogen atom from the toluene methyl group to give ethane and benzylic radical (7):

$$\dot{\mathrm{E}}\mathrm{t} + \mathrm{Et} \rightarrow [\dot{\mathrm{E}}\mathrm{t}\ \dot{\mathrm{E}}\mathrm{t}]^{F}\ (\mathrm{RP3}) \qquad (5)$$



(6)

(7)

Recombination of RP3 gives butane (Table 2) of which the ethyl fragments should show A/E polarization. However, as it was impossible to obtain a complete butane spectrum [14], we compared the butane spectrum obtained with spectra described in literature [15] and found that butane shows A/E polarization. Disproportionation of RP3 gives nonpolarized ethane and ethylene (Table 2), because their protons are magnetically equivalent and their NMR spectra have no multiplet structure. Dissociation of RP3 gives a radical that shows multiplet E/A polarization.

When the reaction is carried out in toluene, however, ethyltoluenes are formed in significant amounts.

The formation of ethyltoluene during the reaction permits us to suggest that the formation of ethylcyclohexadienyl radical proceeds by reaction 6. The formation of such a radical must be analogous to the interaction of methyl [16] or phenyl [17] radicals along with that of hydrogen atom with aromatic substrates. The presence of σ-complex radicals of hydrogen atom with various substituted benzenes was confirmed by ESR [18]. When a σ-complex radical meets an ethyl radical in solution, irrespective of spin an RP4 should form, the spin evolution of which cannot lead to a polarization of ethyl fragment of the σ complex, because the A_H parameters for the protons are $\leqslant 0.1$ mT. Thus, the ethyl fragment of the σ complex has a polarization that formed in the RP3. Disproportionation of the RP4 forms ethyltoluene that shows a polarization of the E/A ethyl fragment and a nonpolarized ethane. Recombination by the RP4 is unlikely because a labile hydrogen atom is present, in the σ-complex, α to the ethyl group.

Some of the ethyl radicals originating from the RP3 react with the initial XeF_2:

$$\dot{E}t + XeF_2 \rightarrow EtF + X\dot{e}F$$

The occurrence of multiply (E/A) polarized signals of ethyl fluoride in ^{1}H NMR spectrum probably accounts for this.

The initial concentration of XeF_2 is about 100 times less than that in toluene, furthermore, XeF_2 is consumed rapidly by interaction with DEEA. So, a polarized ethyl radical reacts mainly with the solvent, and ethyl fluorine is formed only in trace amounts.

Table 2 shows the formation of a small amount of diethyltoluenes when the reaction is carried out in toluene, which is explained by the large yield of ethyltoluene. Consequently the ethyl radicals can form a σ-complex radical with the ethyltoluene formed to give diethyltoluene.

A number of ethyl radicals can take part in the competitive abstraction of hydrogen atom from the solvent (7) to form benzylic radicals. Recombination by the benzyl radicals leads to the formation of dibenzyl, and σ-complex radicals with toluene – and then a to the formation of asymmetric ditolyles; also found among the reaction products.

Thus, the interaction of DEEA and xenon difluoride takes place by a radical mechanism. The main reaction, product $(C_2H_5O)_2AlF$ was formed in the same way as in the interaction either with initial XeF_2 or with $X\dot{e}F$. As a result, many ethyl radicals are formed, the transformation of which determines the polarization on the protons. ^{19}F CIDNP elucidates mainly the heminal processes in the primary RP.

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