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ADDUCTS OF PHENYLACETYLENE WITH ALKALI METALS

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Summary

The interaction between phenylacetylene (PA) and excess alkali metal (lithium, sodium and potassium) in tetrahydrofuran and hexamethylphosphorotriamide at room temperature has been examined. Gas-chromatography and IR and optical spectroscopy show that the metal adducts obtained are the reduced forms of the corresponding phenylacetylenides. The paramagnetic properties of the products and the hyperfine structure of the ESR spectra of the corresponding K and Na adducts confirm their anion-radical character. The metal adducts initiate the polymerization of methyl methacrylate and styrene, and transfer electrons to aromatic hydrocarbons and non-enolizing ketones, their anion-radicals being obtained.

Introduction

The anionic polymerization of monosubstituted acetylenes is a slow reaction, leading to the formation of low molecular weight products (oligomers) [1-4]. The polymerization is preceded by the formation of acetylenide [1,2] or its complexes with the initial acetylene [3,4] irrespective of the kind of initiator.

There are no data in the literature on the polymerization of monosubstituted acetylenes, initiated by initiators of anion-radical type but by analogy with vinyl polymerization it may be expected that the first reaction product would be the anion-radical of phenylacetylene (PA). Because of the conjugation present in the phenylacetylene molecule, the anion-radical is expected to be stable enough to be studied spectroscopically.

In the present work a study of the interaction between PA and alkali metals in aprotic solvents is reported.

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Experimental

PA was obtained from 1,2-dibromoethylbenzene [5] and separated from styrene (St) by converting PA to acetylenide (interaction with sodium in diethyl ether). After washing several times with ether the acetylenide was suspended in benzene and decomposed with water. PA was distilled off from the benzene solution, dried over CaH_2 and redistilled in vacuo. The purity of the PA was checked by gas-chromatography.

The solvents: tetrahydrofuran (THF), hexamethylphosphorotriamide (HMPT), and the monomers: methylmethacrylate (MMA) and styrene were purified in the usual way [6]. The solid components were sublimed and dried in vacuo. All experiments were carried out in vacuo (10^{-4}—10^{-5} mmHg).

The IR spectra of the reaction mixtures were recorded on UR-10 and UR-20 spectrometers (Carl Zeiss, Jena) in cells of KBr (0.25 mm) and NaCl (0.17 mm).

The electronic spectra were recorded on a SPECORD UV VIS (Carl Zeiss, Jena) in quartz cells (0.0317 to 0.99 cm).

Gas-chromatographic analysis of the protonated products was made on "Tsvet-69-6" and "Chrom-3" apparatus.

The ESR spectra were taken on JEOL, JES-3 type, BSX, $x = 3.2$ cm ($H_0 = 3300$ g).

Results and discussion

I. Interaction between PA and alkali metals

When a solution of PA (0.1—0.5 mol/l) in THF is brought into contact with a metal mirror (Na or K) or with lithium cut into small pieces (the ratio metal:PA $>$ 4:1 mol/mol) the metal surface and later the whole solution becomes red. Simultaneously, a light yellow suspension of insoluble phenylacetylenide (PAd) is obtained. With prolonged contact the quantity of the dissolved metal increases and the colour becomes more intense. Because of the heterogeneous character of the process, after 1-2 days the alkalinity and spectral characteristics of the solutions remained constant for several weeks. The rate of the process decreases according to the following sequence: Li $\geqslant$ K $>$ Na. An insignificant dependence of the process on temperature is observed. A decrease of the temperature to —50° C has no observable effect on the process.

The reaction proceeds in two stages: formation of acetylenide at equimolar initial metal:PA ratio (rapid stage) and following interaction with an excess of metal (slow stage). Replacement of THF with HMPT (i.e. increasing the solvating properties and the dielectric constant of the solvent) shortens the process to several minutes. Addition of small amounts of polyethylene oxide (PEO) (Mol. wt. 15 000), which possess a good solvating ability [7], also accelerates the reaction.

II. Properties of the products

Solutions of the products have a brick-red (PA + K) to redviolet (PA + Li) colour. The coloured solutions obtained by interaction of PA with alkali metals (alkalinity 0.005—0.05 mol/l) are sensitive to oxygen, moisture and com-

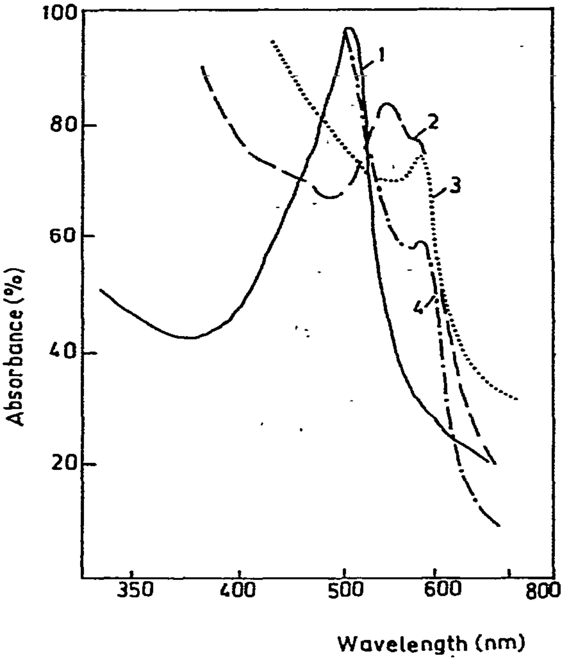

Fig. 1. Absorption spectra of metal adducts: 1 K; 2 Na and 3 Li in THF and 4 Na in HMPT.

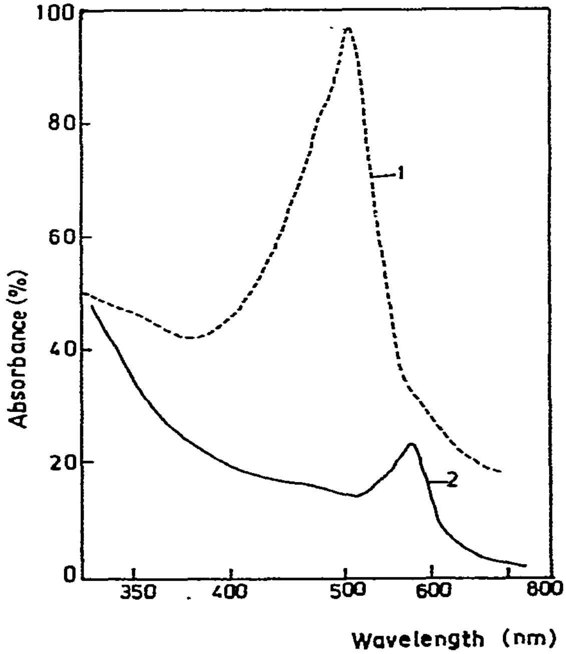

Fig. 2. Absorption spectra of the solutions of PA metal adducts in THF: 1 K; 2 K + PEO.

pounds with an active hydrogen atom. Their electronic spectra are characterised by bands at 490 nm (PA + K), 532 and 562 nm (PA + Na) and 562 nm (PA + Li) which disappear on protonation of the solutions. In the spectrum of the Na-adduct in HMPT, only the band at 562 nm is observed (Fig. 1, curve 4). The presence of PEO (as solvating agent) in the solution of PA + K in THF changes the optical spectrum (Fig. 2) so that only the band at 562 nm is observed. The dependence of the light absorption of the corresponding solutions on the size of the counterion, as well as the observation that the absorption band at 562 nm is independent of the nature of the metal cation, shows that a dynamic equilibrium of different ionic species exists in the solutions.

The solutions of PA metal adducts are paramagnetic (*g*-factor about 2). The ESR spectra of the K-adduct in THF (Fig. 3) and the Na-adduct in HMPT show hyperfine splitting, consisting of 72 lines, while the ESR spectrum of the solution of PA + K in THF, in the presence of PEO, is a singlet without hyperfine structure. Similar "disappearance" of the hyperfine structure of the ESR spectrum is observed in the presence of cryptates and other polyethers [8]. The number of lines in the ESR spectrum corresponds to the theoretical number for the spectrum of the reduced form of PAd containing one unpaired electron. The ESR spectrum of the Na-adduct in THF at room temperature represents a singlet. Lowering the temperature to —45° C induces an additional splitting to about 10 lines.

The characteristic absorption in the visible region and the paramagnetic properties of the solutions, as well as the influence of the medium on them, show that in the interactions of PA with alkali metals, metal adducts of the anion-radical type are obtained.

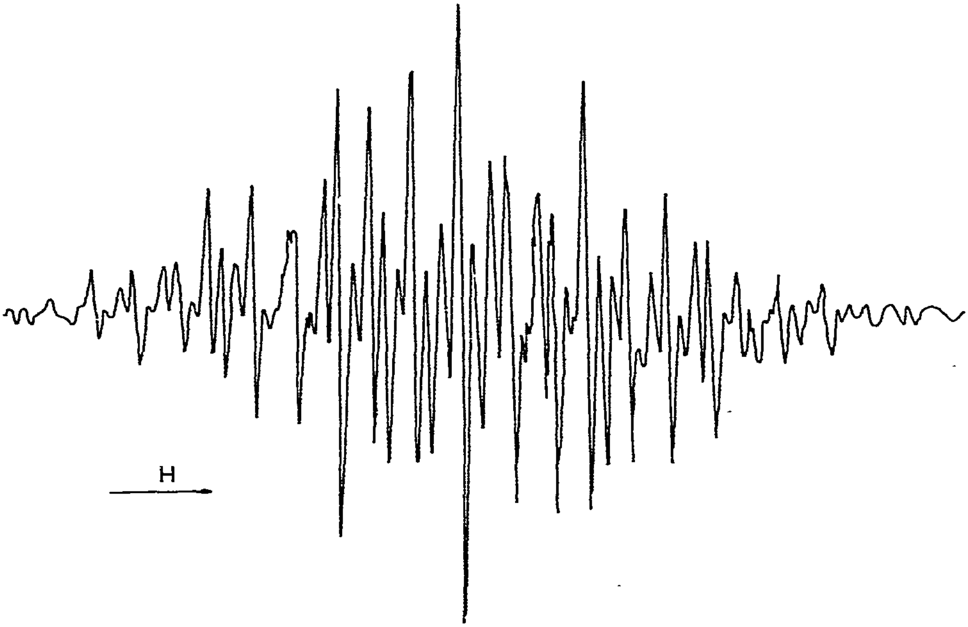

Fig. 3. ESR spectra of K-adduct in THF.

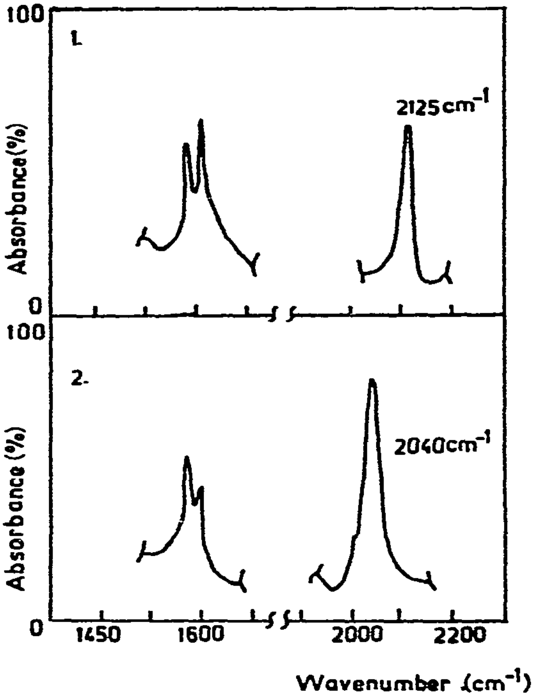

Fig. 4. IR spectra of: 1 PA; 2 Li-adduct in THF.

It is known [9] that the formation of anion-radicals, i.e. the acceptance of an additional electron in the anti-bonding orbital leads to a decrease in the force constants of the corresponding bonds and correspondingly to a decrease in the frequencies of the characteristic bands in the IR spectra, thus the character of the IR spectra can offer proof of their anion-radical nature. The regions of absorption 2200—2000 cm^{-1} and 1600—1500 cm^{-1} were studied. In the IR spectrum of the Li-adduct (Fig. 4) an absorption at 2040 cm^{-1} is observed, i.e. a significant decrease (about 80 cm^{-1}) in the frequency of the band at 2125 cm^{-1}, corresponding to the stretching vibrations of the triple C≡C bond [10], as

TABLE 1

INFLUENCE OF ELECTRON AFFINITY OF AROMATIC COMPOUNDS ON ELECTRON TRANSFER REACTION

Aromatic compounds	Half-wave reduction potential $-E_{1/2}$ (V) [11,12]	Electron affinity ϵ_0 (eV) [12]	Electron transfer reaction
Fluorenone	1.46	—	+
Xanthone	1.58	—	+
4-Benzoyldiphenyl	1.62	—	+
Benzophenone	1.86	—	+
Anthracene	1.94	0.57	+
Chrysene	2.34	0.42	+
Phenanthrene	2.45	0.31	+
Naphthalene	2.50	0.15	—

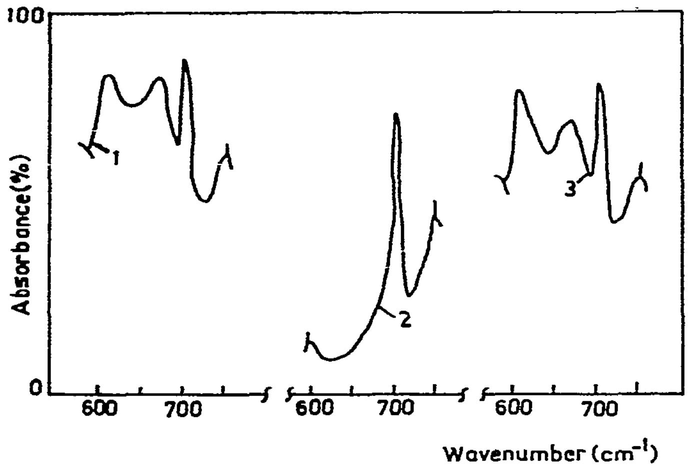

Fig. 5. IR spectra of: 1 PA; 2 K-adduct in THF; 3 protonated products of K-adduct in THF.

well as a change in the frequencies of the vibrations of the C=C bonds in the aromatic nuclei. This confirms the anion-radical nature of the adducts.

The anion-radical character of the PA metal adducts was also established by studying their chemical behaviour.

The addition of the adducts to solutions of a number of aromatic hydrocarbons and non-enolizing ketones results in the formation of the anion-radicals of these compounds. The electron transfer is accomplished immediately after mixing. The influence of the nature of the aromatic compound on the electron transfer reaction is given in Table 1.

The reduced forms of PA are able to transfer electrons to compounds with an electron affinity higher than 0.15 eV, i.e. in the reaction conditions used the adducts are close in their donor-accepting properties to the anion-radicals of naphthalene and phenanthrene. As one would expect, in the interaction of an excess of naphthalene-K in THF with PA, the reverse transfer takes place, i.e. metal adducts of PA are obtained.

In the IR spectra of the saturated adduct solutions no absorption at 700-600 cm^{-1} is observed, although it appears in the spectra of their protonated derivatives (Fig. 5). The bands at 655 and 625 cm^{-1}, characteristic of $\equiv$C—H vibrations in monosubstituted acetylenes, prove that regeneration of PA occurs after protonation of its metal-adduct solutions. No oligomers of PA exist in the protonated products.

The composition of the reaction mixtures after protonation was studied by gas chromatography. Figure 6 shows chromatograms of several metal-adduct solutions after treatment with ethyl alcohol or HCl. All the samples contain PA, which was not present in the initial solutions, as shown by IR spectroscopy (Fig. 5).

The spectral studies show, that in the interaction of PA with alkali metals, monomer dianion-radicals of the type $[PA^{-}Me^{+}]^{\dot{-}}$ Me are obtained. In contrast to the vinyl monomer anion-radicals which are the first product in reaction

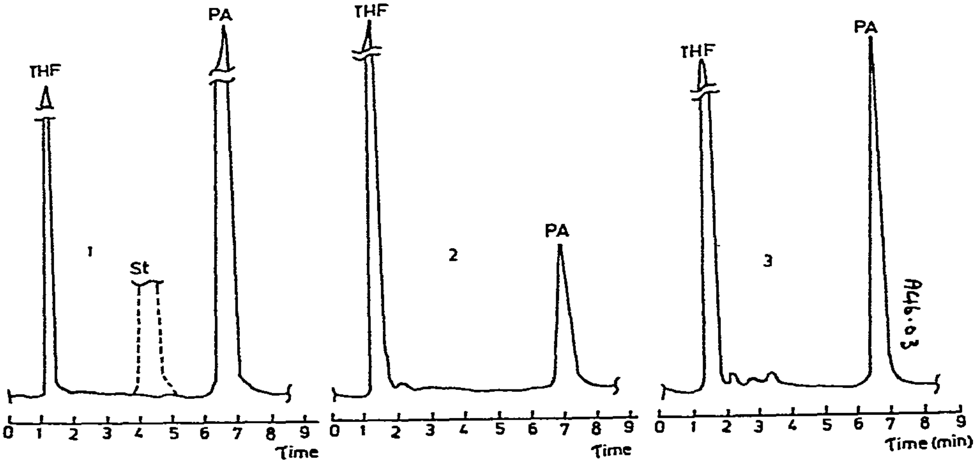

Fig. 6. Gas-chromatograms of: 1 solution of PA in THF; 2 protonated products of K-adduct in THF; 3 protonated products of K-adduct + PEO.

with alkali metals, the adducts obtained cannot dimerize and/or cause further polymerization of the excess of PA. On the other hand, PA metal adducts are able to initiate polymerization and copolymerization of St and MMA in the temperature interval —78 to 25° C.

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