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Abstract

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INVESTIGATION OF THE NATURE OF THE CARBON–ALKALI METAL BOND BY THE METHOD OF ELECTRONIC ABSORPTION SPECTRA

When considering the regularities of the polymerization of hydrocarbon monomers in nonpolar media, initiated by various alkali metals or their organic compounds, a number of assumptions were put forward concerning the nature of the active centers ($^{1-5}$).

At present a considerable number of works have been published in which electronic absorption spectra were used as a method for studying the nature of the Me–C bond ($^{4,6-10}$). However, the results of these investigations were still insufficient for clarifying the possibilities of this method in solving the problem posed. It was established that the electronic spectra of living, nonisomerized polystyrene change little when Li is replaced by Na and K and when going from hydrocarbon media to electron-donor ones (^{4}). Similar results were obtained by us in studying the spectra of certain polydienes (see Table 1).

With the aim of a more detailed investigation of the possibilities of this method for studying the nature of the C–Me bond, in the present work the electronic absorption spectra (e.a.s.) were determined for a series of alkali-metal compounds obtained by polymerization and copolymerization of various monomers (dienes, styrene, 1,1-diphenylethylene, anthracene*), as well as compounds obtained in certain substitution and exchange-decomposition reactions (triphenylmethane, triphenylchloromethane, fluorene), as a function of the nature of the metal and solvent.

Fig. 1. Electronic absorption spectra of substituted allylic carbanions obtained in the polymerization of dienes: **1** –lithium polyisoprene in hexane; **1′** –system "1" with subtraction of polyisoprene; **2** –lithium polybutadiene in THF; **3** –sodium polyisoprene in hexane; **4** –sodium polybutadiene in THF (high concentration of carbanions); **5** –sodium polybutadiene in THF (low concentration of carbanions); **5′** –system "5" with subtraction of polybutadiene; **6** –potassium polyisoprene in THF.

The work was carried out with the aid of an all-fused quartz cuvette on an SF-4 spectrophotometer, using thoroughly purified substances. Most of the monomers and solvents were treated with ethyllithium, followed by their re-

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condensation into the cuvette. The design of the cuvette made it possible to carry out all operations for preparing and diluting solutions under vacuum. The results obtained are given in Table 1 and Figs. 1, 2, 3.

* In work (11) it was shown that anthracene is capable of adding to polystyryl and polybutadienyl carbanions with formation of an anthracenyl carbanion.

Table 1

Absorption spectra of carbanions under various conditions at 25°C

No.	Medium	Me–R	λ_{max} of carbanion, mμ	λ_{max} of carbanion isomerization products, mμ	Note
1	Benzene	Li-polystyrene	333	430–460; 530–560 very low intensity	Frequencies of the isomerized carbanion are noticeable at high solution concentration

No.	Medium	Me–R	λ_{max} of carbanion, mμ	λ_{max} of carbanion isomerization products, mμ	Note
2	THF	Benzyllithium	330	375	375 mμ after 3 days
3	Benzene	Li(α)-methylstyryl carbanion	338		Obtained by interaction of methylstyrene with LiEt
4	THF	K-α-methylstyryl carbanion	330		
5	Benzene	Na-polystyrene	335–340	400–450	With time the intensity of $\lambda_{max} =$ 335–340 falls, the remainder increases
6	Hexane	Li-polyisoprene	276		
7	Hexane	Na-polyisoprene	–	306	The band is broad, covering a large region of wavelengths
8	Hexane	Li-polybutadiene	276		
9	Hexane	Na-polybutadiene		300–320	Same
10	THF	Li-polybutadieneLi-polyisoprene	280–310		Diffuse maximum

No.	Medium	Me–R	λ_{max} of carbanion, mμ	λ_{max} of carbanion isomerization products, mμ	Note
11	THF	K-polybutadiene	—	235, 375 *	
12	THF	K-polyisoprene	280 (weak intensity)	—	After addition to 11 of isoprene
13	Hexane	$C_3H_7(C_6H_5)_2C$—Li	410 **		
14	Benzene***	$C_3H_7(C_6H_5)_2C$—Li	420		
15	Amine	$C_3H_7(C_6H_5)_2C$—Li	435		
16a	Hexane + 0.2% THF	~ $CH_2(C_6H_5)_2C$—Li	440		Obtained by addition of 1,1-diphenylethylene to lithiopolybutadiene
16b	THF	~ $CH_2(C_6H_5)_2C$—Li	490 **		
17	Toluene	~ $CH_2(C_6H_5)_2C$—Na	460		Obtained by addition of 1,1-diphenylethylene to Na-polybutadiene
18	Benzene	~ CH_2—CH (C_6H_4) HC—Li (C_6H_4)	420	—	Obtained by addition of anthracene to lithiopolystyrene
19	Benzene	—Na	445		

No.	Medium	Me–R	$\lambda_{\max}$ of carbanion, mμ	$\lambda_{\max}$ of carbanion isomerization products, mμ	Note
20	THF	–Na	445	–	Obtained by addition of anthracene to Na-polybutadiene
21	Amine	$(C_6H_5)_3C—Li$	440		
22	THF + amine	$(C_6H_5)_3C—Li$	440 (weak)500 (int.)		Obtained by addition of anthracene to Na-polystyrene
23	Benzene	$(C_6H_5)_3C—Na$	472		
24	THF	$(C_6H_5)_3C—Na$	490		
25	Benzene	$(C_6H_5)_3C—K$	490–500		
26	Benzene	Fluorenyllithium	450 (int.)480 –530 (less int.)		
27	THF + benzene	Li-fluorenyl	454,487 (int.)520, 554 (less int.)		
28	Benzene	Experiment No. 27 after prolonged evacuation	415,440 (int.)470 (less int.)		

* λ 375 mμ was also observed in work (7), where it was assigned to the main, nonisomerized alkyl carbanion.

** Similar data were obtained in our laboratory by A. A. Arest-Yakubovich and in works (16, 17).

*** The shift of $\lambda_{\max}$ upon replacing heptane by benzene confirms the earlier

Fig. 2. Electronic absorption spectra of carbanions of 1,1-diphenylalkyl with counterions: 1 —lithium in hexane medium, 2 —lithium in benzene medium, 3 —lithium in triethylamine medium, 4 —sodium in THF medium, 5 —lithium in THF medium

Figure 2: Fig. 2. Electronic absorption spectra of carbanions of 1,1-diphenylalkyl with counterions: 1 —lithium in hexane medium, 2 —lithium in benzene medium, 3 —lithium in triethylamine medium, 4 —sodium in THF medium, 5 —lithium in THF medium

suggestion (12), made in the study of the kinetics of butadiene polymerization in such media, concerning the formation of complexes of aromatic compounds (toluene, benzene) with organolithium compounds.

From the data of Table 1, Nos. 1, 2, 3, 4, 5, 6, 8, 10, 12, it follows that the electronic spectra of nonisomerized living polymers of styrene, isoprene, and butadiene are practically independent of the nature of the metal (Li, Na, K) and do not change on going from hydrocarbon media to electron-donor media. However, in studying the spectra of the corresponding compounds of triphenylmethyl, 1,1-diphenylalkyl, as well as fluorenyl and alkyl-9-dihydroanthracenyl with metals, a noticeable displacement of the absorption bands and a change in their intensity were found, depending on the nature of the alkali metal and of the medium (Table 1, Nos. 14–28). The sharpest effects are observed for the lithium, sodium, and potassium compounds of triphenylmethyl and diphenylalkyl. The influence of the nature of the metal and of the medium on the spectra is less pronounced in the case of alkyl-9-dihydroanthracenyl and fluorenyl compounds, in which the position of the phenyl groups is fixed by additional bonds.

Fig. 2. Electronic absorption spectra of carbanions of 1,1-diphenylalkyl with counterions: 1 —lithium in hexane medium, 2 —lithium in benzene medium, 3 —lithium in triethylamine medium, 4 —sodium in THF medium, 5 —lithium in THF medium

It is of interest to note that, in the spectrophotometric study of the kinetics of the synthesis of $(C_6H_5)_3CK$ from $(C_6H_5)_3CCl$ and K, along with λ_{max} of the radical $(C_6H_5)_3C$ (345 mµ), which is an intermediate product in the formation of the anion, an intense band with λ_{max} 368 mµ is observed. From the kinetics of the change in band intensity it is seen that the radical passes into a compound with λ_{max} 368 mµ, which is then transformed into a carbanion with λ_{max} 415 and 495 mµ. The nature of the compound having λ_{max} 368 mµ is not clear.

According to previously obtained data (^{1,12,13}), additions of triethylamine (TEA) in a hydrocarbon medium, less sharply than addition of tetrahydrofuran (THF), increase the rate of polymerization and the fraction of structures corresponding to an anionic process. The reasons for such a difference in the influence of these electron-donor additives could not be explained solely by an increase in the dielectric constant of the medium on going from TEA (3.15 at 27°) to THF (6 at 27°).

As follows from the results obtained (Table 1, Nos. 15, 16a, 16b, Fig. 3), the difference cited is apparently due to a considerable extent to the fact that complexes of organometallic compounds with triethylamine molecules, because of steric hindrance, contain a smaller number of solvating-additive molecules than do complexes with THF under the same conditions.

Indeed, as follows from the results obtained, the electronic spectrum of diphenylalkyllithium in the presence of small additions of THF (λ_{max} 440 mμ) is close to the electronic spectrum of the same organometallic compound in TEA medium (λ_{max} 437 mμ). The increase in λ_{max} with increasing THF concentration and with lowering of the temperature (490 mμ) indicates that, under these conditions, the number of THF molecules bound in the complex with diphenylalkyllithium has increased, which has caused a greater polarization of the Me—C bond. From the data obtained, the heat effect of this transition is $\simeq 8 \pm 1$ kcal/mole. It may be thought that the low sensitivity of the electronic-spectra method to a change in the state of the Me—C bond upon changing the nature of the medium and of the alkali metal for polystyryl and polydienyl compounds of these metals is the result of structural features of these systems. Thus, the difference in the λ_{max} value on going from the electronic spectrum of the hydrocarbon (modeling the case of absence of polarization of the Me—C bond) to the carbanion is considerably higher for 1,1-diphenylalkyl hydrocarbons and triphenylmethane than for toluene and olefins. For 1,1-diphenylethane these values are, respectively, 270 mμ (1,1-diphenylethane) and 490 mμ (carbanion of 1,1-diphenylethane), while for toluene they are 275 mμ (toluene) and 336 mμ (benzyl carbanion).

In connection with this, the sensitivity of the electronic-absorption-spectroscopy method for investigating the nature of the Me—C bond in derivatives of 1,1-diphenylalkyl hydrocarbons and triphenylmethane is higher than for polystyryl or polydienyl organometallic compounds. The mechanism of these phenomena can possibly be explained as follows. A change in the nature of the metal and of the medium is accompanied by a change in the charge on carbon, which in turn changes the conjugation energy in the molecule. In the case of conjugation of a negatively charged carbon with one substituent, these changes, as experiment shows (Table 1, Nos. 1, 5, 8, 10, 12), are the same for the ground and excited states. In the case of conjugation of a negatively charged carbon with two or more substituents (Table 1, Nos. 13—17, 21—25), a change in the ground state leads to a change in the valence angle between the substituents (an sp^3 state is admixed to the sp^2 hybridization in the carbanion), which substantially affects the difference between the levels of the ground and excited states, i.e., leads to a dependence of the absorption band on the polarity of the C—Me bond. Fixing the position of two substituents by additional bonds (Table 1, Nos. 18—20, 26, 27) reduces the change in the valence angles and accordingly stabilizes the position of the absorption band. Some role in the electronic spectra of the systems studied is possibly also played by their mutual association, which,

Fig. 3. Electronic absorption spectra

Figure 3: Fig. 3. Electronic absorption spectra

owing to steric hindrance, is probably less pronounced in polynuclear aromatic compounds.

Fig. 3. Electronic absorption spectra of 1,1-diphenylalkyllithium, obtained by addition of 1,1-diphenylethylene to lithium polydienyl, in various media:
1 –hexane (shift of $\lambda_{\max}$ from 410 mμ (see Table 1, No. 13) to 425 mμ in the given system is apparently due to solvation of lithium by the double bonds of the polydiene chain);
2 –hexane + 0.04 vol.% THF, t 25°;
3 –hexane + 0.35 ÷ 3.5 vol.% THF, t 25°;
4 –hexane + 3.5 vol.% THF, $t = -55°$;
5 –hexane + 3.5 vol.% THF, $t = -80°$.

The results obtained support the view that the polarity of the C–Me bond varies under different conditions, and that its dissociation into an ion pair in hydrocarbon media is of low probability.

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