STABILITY OF TETRAMER α-METHYLSTYRENE DIANION IN TETRAHYDROFURAN

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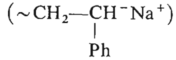
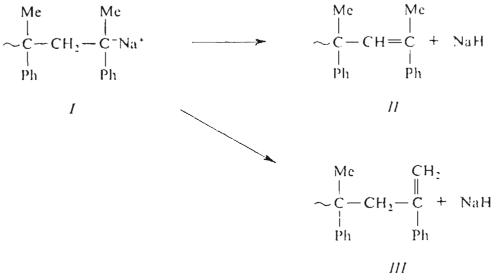
Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Solutions of carbanions of living α-methylstyrene tetramer in tetrahydrofuran exhibit limited stability even at relatively low temperatures. The rate of decay of these active centers depends upon the type of counter-ion and it decreases in the sequence $Li^+ < Na^+ < K^+$. It is dependent also upon temperature, concentration and some other unrevealed factors. In dark, with Na^+ as a counter-ion at 263 K and $\sim C^-Na^+$ concentration of 1·5 mmol/dm^3, the initial period of a fast concentration decrease of active centers is followed by a very slow period of rate decay. At 296 K the decrease of their concentration is much faster and seems to obey a first reaction order.

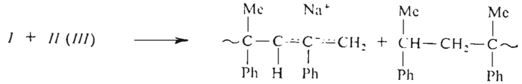
Rinsing the dry inner surface of glass apparatus by solutions of carbanions does not cause a decrease of their concentration. When a part of the glass apparatus is heated up to the softening point, a certain portion of carbanions is consumed.

The α-methylstyrene oligomeric dianions, particularly the tetramer (DIA) have long been a matter of considerable interest of several research teams. The latter is frequently employed as an initiator of anionic polymerization, the carbanions which it contains being considered as a good model of a living end of polymerizing monomer. The spectrum of α-methylstyrene carbanion in near UV and visible region permits direct photometric studies of the behaviour of living centres of polymerization.

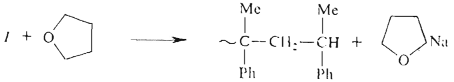
Levy and coworkers followed the spectrophotometrical changes of styrene carbanion solutions as a function of time[1]. Spach, Levy and Szwarc described the behaviour of carbanions derived from styrene and its oligomers  $(\sim CH_2—\underset{\displaystyle Ph}{\underset{|}{C}}H^-Na^+)$ in tetrahydrofuran at room temperature[2]. The authors observed that this carbanion is slowly transformed to NaH and polystyrene with an end double bond. Schmitt has applied this observation to the α-methylstyrene oligomeric anions and postulated the following reactions[3].



(A)



(B)



(C)

Böhm with coworkers have found a discrepancy between the concentration of growing centres (α-methylstyrenecarbanions) determined spectroscopically and from the molecular mass of resulting living polymers initiated by these ions[4]. Richards and Williams examined the structure of DIA (ref.[5]). Comyn and Glasse[6] made an important contribution when finding the involvement of light in reactions of carbanions. They observed the shift of absorption at 340 nm towards longer wavelengths. At the same time the overall absorption of solutions was decreasing. These results, however are not in accordance with other authors[7].

From the known facts concerning the reactions of styrene and α-methylstyrene carbanions it follows that the behaviour of these carbanions is not fully understood.

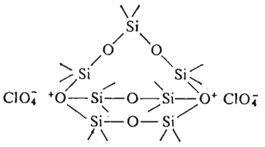
It is surprising that all the authors who have so far examined the behaviour of these reactive species worked at ambient or even at higher temperatures. Neither the role of THF has been sufficiently appreciated namely during the studies and interpretation of spectral data. One of the subsequent products of reaction (*C*) is an alkoxy-ion[3]. The scission of THF ring by strong bases has been described[8–10]. Little is known about the rate and mechanism of these reactions in connection with solutions of DIA in THF.

The α-methylstyrene dianion has recently attracted our attention because of its ability to effect the transformation of polymerization centres (cationic →anionic) and to enable the combination of macroions. It is a purpose of this communication to complement the available data concerning the decay of carbanion absorption in DIA at 343 nm as measured *i*) directly after the formation of DIA; *ii*) at temperatures below 298 K; *iii*) at different types of counter-ions.

EXPERIMENTAL

Chemicals

Tetrahydrofuran, pure, product of Laborchemie Apolda, GDR or Reachim, USSR; it was predried prior to use over metallic sodium and then distilled twice in vacuo from a green solution of naphthalene sodium. α-Methylstyrene, pure, product of Kaučuk, Kralupy, Czechoslovakia, was purified from stabilizer by shaking with aqueous 15% KOH, washed with water to neutral reaction of water phase, predried with $CaCl_2$ and distilled twice over CaH_2. The preparation of the silenium dicationic initiator (DIC),



IV

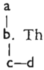
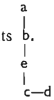
was described earlier[11]. The preparation of tetramer α-methylstyrene dianion (DIA) has already been described[12]; it is based on the reaction of monomer with freshly distilled Na in THF at 250 K. Alkali metals, product of Lachema, Czechoslovakia, were freed from impurities by a mechanical removal of the surface layer in an inert atmosphere. Sodium which used in most cases was distilled on a high-vacuum line.

Apparatus and Procedures

All operations were carried out on a high-vacuum line except for handling of initiators which were syringed under dry nitrogen. Reactors were sealed to a high-vacuum line and dried for 6 h at $10^{-3}-10^{-4}$ Pa with an occassional heating at about 600 K.

The spectra of DIA at 343 nm were measured (D = absorbance) on a Perkin-Elmer 330 spectrophotometer using 1 mm quartz cells.

Reactor for spectrophotometry of DIA stock solution was composed of elements  $\begin{array}{l} \text{a} \\ | \\ \text{c—d} \end{array}$ (Fig. 1).

Formation and decay of carbanions were monitored through spectrophotometry in reactor composed of elements  $\begin{array}{l} \text{a} \\ | \\ \text{b} \\ | \\ \text{c—d} \end{array}$. The influence of seal-off was studied in a set of elements  $\begin{array}{l} \text{a} \\ | \\ \text{b} \\ | \\ \text{e} \\ | \\ \text{c—d} \end{array}$.

Apparatus for neutralization of DIC by DIA consisted of elements $\overset{\overset{a}{|}}{c}$ and $\overset{\overset{a}{|}}{c}—f—\overset{\overset{a}{|}}{c}$. The manipulation with DIA was described in the previous report[12].

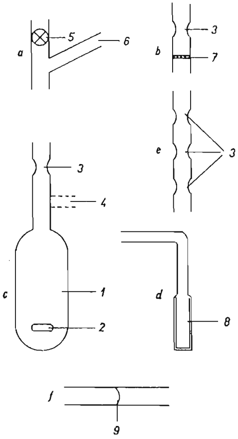


FIG. 1

Elements for assembling reactors: **1** reaction or storage bulb, **2** stirring bar, **3** seal-off points, **4** attachment for quartz cell or for element **f**, **5** two way stopcock, **6** high vacuum line attachment, **7** sintered glass, **8** quartz cell, **9** break seal

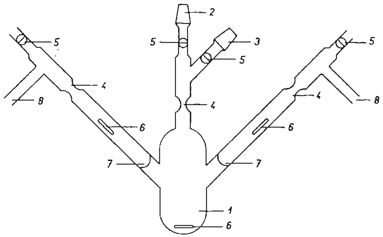


FIG. 2

Storage vessel for DIC: **1** bulb for DIC, **2** high-vacuum line attachment, **3** sampling point for DIC, **4** seal-off point, **5** two-way stopcock, **6** stirring bar, **7** break-seal

For the dication preparation the reactor in Fig. 2 was employed. The apparatus served for the final stages of the DIC synthesis (to remove residual reaction water and chlorides)[11] and for storage and sampling of the initiator.

UV Spectrophotometry of Dia

Influence of counter-ion. The alkali metal (Li, Na, K) was placed into the space above sintered glass **7** (the reactor from elements a—b—c—d; see the respective text of the Experimental part) under nitrogen and the reactor was vacuum dried. THF (20 cm^3) and α-methylstyrene (2 cm^3) were distilled into the reactor, which was sealed-off at point b3 and the metal was allowed to react with the solution at 263 K. Then the reactor was sealed-off at point c3 and the concentration of DIA was measured.

Influence of temperature. A desired portion of freshly prepared DIA was syringed from a storage flask into a predried part of the reactor (a—c—d). THF (20 cm^3) was distilled in, the reactor was sealed-off at point 3 and stored at desired temperature. The absorbance of solution was measured periodically at 343 and 420 nm.

Influence of sealing-off glass reactors. THF (20 cm^3) and α-methylstyrene (0·1 cm^3) were distilled into the dry reactor (a—b—e—c—d). The reactor was then filled with pure nitrogen, a small chip of alkali metal was then placed on the sintered glass disc b7 and the reactor was sealed-off the line at point b3. After thermostating the whole set-up to a desired temperature the solution of monomer was transferred into the space containing the metal. When the selected concentration of DIA was reached the part b was sealed-off at higher part of constriction e3. The spectrum was taken after the temperature was established and then again after washing the whole internal surface with the solution of DIA and after each seal-off operation at e3.

Neutralization of DIC *by* DIA. After vacuum drying of bulb **1** at the suited apparatus (a—c), DIC was syringed, a desired portion of THF was distilled in. DIA was added and a colour change was monitored.

Combination of polymeric dication of THF *with various concentrations of* DIA. DIC was syringed into bulb **1** at the convenient apparatus (a—c—f—c—a), THF was distilled in, the reactor was sealed-off at point c3 and the content polymerized at 263 K. A desired amount of THF was distilled into vacuum dried second bulb of the apparatus and DIA was added. After sealing-off the reactor the contents were mixed at 263 K after breaking the seal **g** and the colour changes were monitored.

RESULTS AND DISCUSSION

UV spectrum of tetramer α-methylstyrene dianion (DIA) is characteristic only within the 200—500 nm range. The peak at 343 nm was assigned to carbanion[13]. Thus, the decrease of absorbance at 343 nm was considered as the criterion of carbanion stability.

UV *Spectrometry of* DIA *Immediately after Preparation*

We measured the spectrum of the initiator prepared directly in the reactor connected to the cell. At the beginning, the surface area of metal is coloured by the anion formed and the colour disappears upon shaking. The observed initial decay of DIA is probably due to a reaction of a minute part of DIA with THF. After a measureable absorbance of solution was reached (*c.* 2 mmol/dm^3 carbanions), the part of reactor

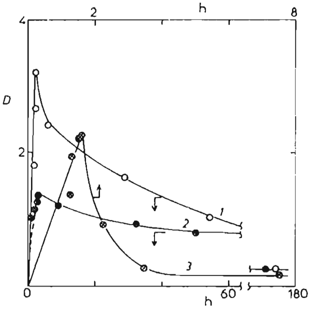


FIG. 3

Time dependence of formation and decay of DIA: ○ Li$^+$, 263 K; ⊗ Li$^+$, 296 K; ● Na$^+$, 296 K. Concentration of the active centers: 0—1·5 mmol/dm^3; *D* — absorbance

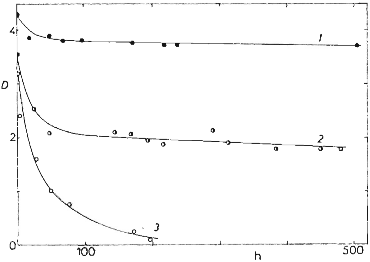


FIG. 4

Time dependence of decay of DIA with Li$^+$ (○), Na$^+$ (◑) and K$^+$ (●) counter-ions at 263 K. Concentration of the active centers: 0—2 mmol/dm^3; *D* — absorbance

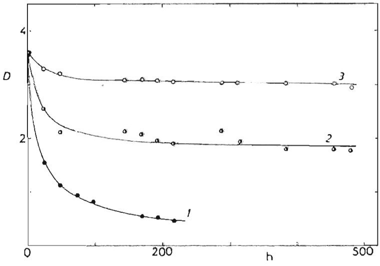


FIG. 5

Influence of temperature on the decay of DIA with Na$^+$ counterion. Temperature (K): ○ 253, ◑ 263, ● 296; concentration of the active centers: 0—1·5 mmol/dm^3; *D* — absorbance

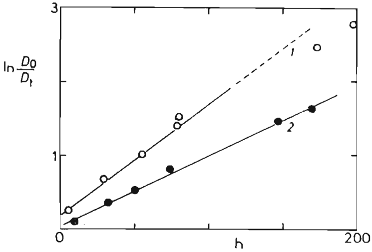


FIG. 6

Decay of DIA as a first order reaction. Counter ion (temperature): ○ Li$^+$ (263 K), ● Na$^+$ (296 K); concentration of the active centers: 0—2 mmol/dm^3; D_0 — absorbance in $t = 0$, D_t — absorbance in $t \neq 0$

with an alkali metal was sealed-off and the decrease of DIA concentration with time was measured. The results are presented in Fig. 3.

Influence of Counter-Ion

Ionic radii of alkali metals in gas phase increase in sequence $Li^+ < Na^+ < K^+$ (ref.[14]) and reactivity of their compounds usually increases in the same sequence. When considering the reactivity of ion pairs in THF it is better to take into account the Stokes radii which involve the solvating envelope of ions[15]. In this case the sequence of reactivity is reversed. The experimental data shown in Fig. 4 indicate the highest stability of DIA with K^+ counter-ion, thus confirming the above statement. The values of Stokes radii increase in sequence $K^+ < Na^+ < Li^+$, the same sequence being observed for an increase of $k_{p\pm}$ in the polymerization of styrene in THF (ref.[13]) ($k_{p\pm}$ is the rate constant of propagation on ion pairs).

Temperature

There is a significant influence of temperature on the stability of DIA. This follows from Fig. 5. At higher temperatures the decay of centres seems to be pseudomonomolecular (Fig. 6).

Influence of Sealing-off

Drying of reactors at room temperature employing the described evacuation on a high-vacuum line is quite sufficient for some experiments. It was proved by flushing the whole internal surface of the reactor. A substantial decrease of absorbance

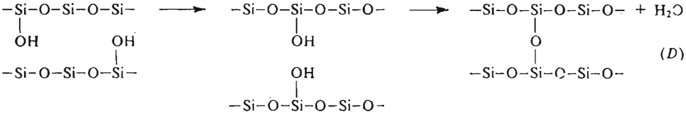
TABLE I

Neutralization of DIC by disodium α-methylstyrene tetramer (0·03 mmol of DIC in 20 cm^3 of THF) at different temperature of mixing. Resulting colour: A-red, B-orange, C-colourless

T K	Excess of DIA, %			
	0	20	40	100
203	C	B	A	A
203[a]	C	B	B	A
203[b]	C	C	B	A
263	C	C	C	A
273	C	C	C	A
296	C	C	C	A

[a] $\bar{M}_n$ of polymerizing THF (after one day at 263 K) was 2 000. [b] DIC in 40 cm^3 of THF.

does not take place, the concentration of DIA remaining constant. Heating of glass above the softening point probably releases the bonded (and thus unreactive) water. Water may be formed through condensation of silanol groups migrating from deeper layers of glass to the surface at higher temperatures.


(D)

The amount of released water corresponds to about 10^{-5} mole of DIA per one sealing-off operation under our conditions. Measurements were performed at 263 K within one hour using a solution of 1·5 mmol/dm^3 DIA with Na$^+$ counter-ion stored 24 h after its preparation.

Number of sealing-off's:	1	2	3	4
Absorbance (*D* at 343 nm):	3·80	3·61	2·10	1·85

Neutralization of DIC *by* DIA

Tables I and II summarize the colour changes by neutralization of DIC (the initiator or dicationic polymer of THF) by DIA with Na$^+$ counter-ion. The results indicate

TABLE II

Neutralization of dicationic poly(tetrahydrofuran) (0·02 mmol of oxonium ends in 20cm^3 of THF) by 100% excess of the carbanions of disodium α-methylstyrene tetramer dissolved in different amount of THF at 203 K (temperature of mixing). Resulting colour: A-red, B-orange, C-colourless

$\overline{M}_n$ of polymer	THF in DIA mmol	Resulting colour
12 000	27·4	C
8 000	26·4	C
10 000	20·5	B
10 000	17·4	B[a]
10 000	19·5	A
12 000	19·5	A

[a] Temperature of mixing 263 K.

that the concentration decrease of carbanions during their reaction with the carboxonium ions is a function of the concentration of reacting anions. The reason for this phenomenon is being investigated[16].

If the absorbance at 343 nm is an indicator of existence of a living carbanion (it is likely, though not proved directly), then a solutio nof disodium tetra(α-methylstyrene) in THF with the concentration of 2 mmol/dm^3 is stable enough within the interval 2 – 14 days, if stored in dark and in strictly inert medium at 263 K. The same is valid for the case of DIA containing K$^+$ counter-ions. Living anions with Li$^+$ counter-ions are unstable under the same conditions.

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