AN INFRARED STUDY OF INTERACTIONS IN THE SYSTEM SODIUM tert-BUTOXIDE–TETRAHYDROFURAN

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Dedicated to Academician O. Wichterle on the occasion of his 75th birthday.

The adduct of sodium tert-butoxide (t-BuONa) with tetrahydrofuran (THF) was studied by measuring changes of infrared spectra in the range $900-1\ 100\ cm^{-1}$. Alkoxide autoassociation and solvation of this associate by tetrahydrofuran play a role in adduct formation. In hydrocarbon solvents in the presence of minor amounts of THF, higher t-BuONa associates are dissociated, the preferred form being a tetramer solvated by three THF molecules. At large excess of THF, the tetramer is solvated by four THF molecules. The stability constant of the adduct, referred to one Na—O bond, is 5·01.

Alkali metal alkoxides can act as initiators of anionic polymerizations[1]. It is assumed that the polymerization e.g. of methyl methacrylate is started by a reaction of the ester with the alkali alkoxide, yielding an active centre which then increases its molecular mass by the addition of further monomer units. In solvating solvents, e.g. in tetrahydrofuran (THF), this reaction proceeds at a higher rate than in hydrocarbons, and with a different contribution of the various partial reactions. The effect of THF is interpreted as solvation of the alkali metal, with adduct formation.

In this work, the generation and nature of one of these adducts was studied, namely of sodium tert-butoxide (t-BuONa) with THF. The existence of this molecular adduct was established by preparative methods[2] and by means of infrared spectra[3]. Two competing processes are involved in its formation — solvation of the t-BuONa molecule (specifically by THF), and autoassociation of the alkoxide. By molecular mass determination in cyclohexane solution, the degree of t-BuONa association was found to be 8·2 (ref.[4]). Due to solvation, the degree of association in THF solution decreases to 3·9 (ref.[4]). Dipole moment measurements revealed[5] that the structural unit in THF solution is highly symmetrical. It is assumed[4] that the most suitable schematic structure of the adduct has the form of a cube, with oxygen and sodium atoms alternating at its vertices. This hypothesis is supported by the analogy with t-BuOK, the crystals of which exhibit a similar structure[6]. However, the structure of t-BuONa in the crystalline state is more complicated. By X-ray measurements, Weiss could show that the unit cell of t-BuONa is composed of hexameric

and nonameric associates in the ratio 1 : 1 (refs[7,8]). This would yield a mean degree of association equal to 7·5, in fairly good agreement with the association degree of t-BuONa found in cyclohexane solution. Therefore it is possible that t-BuONa in hydrocarbon solvents forms similar structures as in the solid state.

EXPERIMENTAL

Sodium tert-butoxide (t-BuONa) was prepared according to ref.[3]. Tetrahydrofuran (THF) and the used solvents were specially dried and purified. THF was column distilled with sodium, and redistilled in argon atmosphere with Na-anthracene, prior to use. Cyclohexane was shaken with a nitration mixture at 50°C. After washing and drying with calcium chloride it was column distilled. The middle fraction was filtered through active silica gel and dried by distillation with $LiAlH_4$. Heptane was shaken twice with 10% of a mixture of $P_2O_5 + H_2SO_4$, dried with calcium chloride and rectified with $LiAlH_4$.

All operations, including preparation of solutions and filling of IR measuring cells, were performed in inert atmosphere of purified argon, using special three-way cocks[9].

IR spectra in the range $900 - 1\,100\ cm^{-1}$ were measured with the spectrometers Zeiss UR 10, Perkin–Elmer 221 and Perkin–Elmer 457. For spectral studies of the temperature dependence of adduct formation in the range -65 to $+55°C$, the low-temperature equipment VLT-2 (RIIC) was used. During the experiment, the temperature in the cell was followed by means of a thermocouple. The overlapping bands at $1\,057$ and $1\,073\ cm^{-1}$ were separated using the ELLIOT 503 computer, assuming Lorentzian shapes. Other bands were separated directly in the spectra, assuming symmetrical bands shapes.

Determination of molar absorbance coefficients: The absorbance coefficient of the band of free THF at $1\,073\ cm^{-1}$ (ε_{TF}) was determined by tetrahydrofuran calibration in cyclohexane solution, $\varepsilon_{TF} = 210\ l\ mol^{-1}\ cm^{-1}$.

The determination of the absorbance coefficient of the band at $1\,057\ cm^{-1}$ corresponding to THF bound in the adduct (ε_{TAD}) was based on the assumed equilibrium between free and bound THF in solution[10], $\varepsilon_{TAD} = 260\ l\ mol^{-1}\ cm^{-1}$.

The absorbance coefficient of the band of tetrameric alkoxide at $978\ cm^{-1}$ was determined in cyclohexane solution in the presence of excess THF. Under these conditions, t-BuONa is present in tetramer form of concentration $c_{tetra} = c_{BO}/4$ where c_{BO} is the initial t-BuONa concentration; $\varepsilon_{tetra} = 340\ l\ mol^{-1}\ cm^{-1}$.

RESULTS AND DISCUSSION

Solvation of Sodium tert-Butoxide by Tetrahydrofuran

The formation of the t-BuONa–THF adduct was followed by IR spectroscopy, from spectral changes in the range $900 - 1\,100\ cm^{-1}$ (see Fig. 1). The presence of t-BuONa leads to a shift of the THF band at $1\,073\ cm^{-1}$ to a lower wavenumber, $1\,057\ cm^{-1}$. This band is assigned to the C—O stretching vibration, and the lowering of its wavenumber corresponds to the interaction of THF with the alkoxide. The band at $1\,073\ cm^{-1}$ corresponds to free THF, and the band at $1\,057\ cm^{-1}$ to THF

bound in the adduct. While these bands are characteristic of THF changes by solvate formation, the spectral range between $950-980$ cm^{-1} contains information on alkoxide structure. Absorption bands in this range probably correspond to a CH$_3$ rocking vibration interacting with C—C and C—O stretching vibrations of the alkoxide[11]. In cyclohexane solution, where t-BuONa is present in the form of an associate of mean association degree, x, 8·2 (ref.[4]), the spectrum exhibits two bands with maxima at 956, 965 cm^{-1}, and a shoulder at 969 cm^{-1}. In the presence of THF the original associates decompose yielding a tetramer[4]; in the spectrum this is manifested by the appearance of a new band with a maximum at 978 cm^{-1}, at the expense of the bands between $950-970$ cm^{-1}. The band at 978 cm^{-1} can be assigned to the t-BuONa tetramer, and the bands at 956, 965, and 969 cm^{-1} to the higher associates. Consequently with increasing degree of association the corresponding band is shifted towards lower wavenumber. A similar effect was also observed with the mixed alkoxide, sodium methoxide/tert-butoxide[12], and also with lithium methoxide[13]. For the determination of the equilibrium concentrations of the system components, the molar absorbance coefficients of the corresponding absorption bands have been determined (see Experimental).

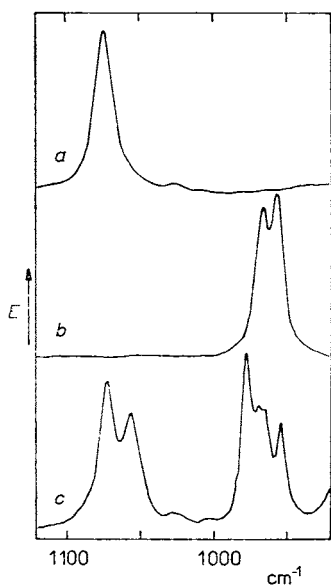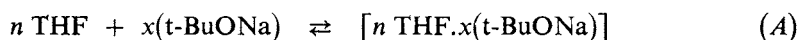Adduct formation may be assumed to follow the equilibrium

$$n \text{ THF} + x(\text{t-BuONa}) \rightleftarrows [n \text{ THF}.x(\text{t-BuONa})] \qquad (A)$$

FIG. 1

Infrared spectra characterizing the system tetrahydrofuran (THF)–sodium tert-butoxide (t-BuONa) in cyclohexane solution a THF, b t-BuONa, c THF + t-BuONa

where the expression in square brackets designates the adduct. Upon mixing of THF with t-BuONa it was found that at a constant molar ratio of the starting components the ratio of the equilibrium concentrations of bound and free THF considerably depends on the overall concentration of the solution. With increasing concentration the band of bound THF $(1\ 057\ cm^{-1})$ grows at the expense of the band of free THF $(1\ 073\ cm^{-1})$ and also the tetramer band at $978\ cm^{-1}$ grows with a simultaneous decrease of the bands in the range $950 - 970\ cm^{-1}$, corresponding to higher associates (see Fig. 2). Lowering of temperature has a similar effect as the increase of solution concentration. These results indicate that at increasing THF and t-BuONa concentrations (or decreasing temperature) the equilibrium (A) is shifted in favour of the adduct. The apparent concentration dependence of the equilibrium constant signifies that adduct formation is not controlled by a simple equilibrium, but rather is a result of a complicated system of partial equilibria.

Alkoxide Autoassociation

We have assumed that the observed equilibrium shift could be connected with a concentration or temperature dependence of alkoxide autoassociation, affecting adduct formation. Therefore we have followed the dependence of t-BuONa association in cyclohexane solution on concentration and temperature. A mixed solvent, cyclohexane–heptane $(3 : 2)$ was used for measurements at low temperatures. Fig. 3 shows the relative growth of the bands at 965 and $969\ cm^{-1}$ at the expense of the band at $956\ cm^{-1}$ with decreasing solution concentration, or with increasing temperature.
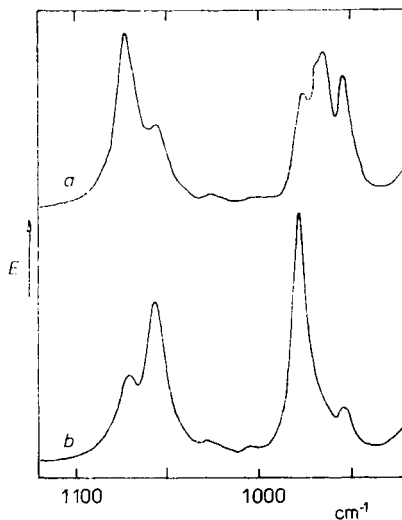

FIG. 2

Infrared spectra of the system THF–t–BuONa in cyclohexane solutions: *a* $c_{TO} = c_{BO} = 0.150\ mol\ l^{-1}$, *b* $c_{TO} = c_{BO} = 0.750\ mol\ l^{-1}$; c_{TO}, c_{BO} are the initial concentration of THF and t-BuONa, respectively

The separation of the bands at 965 and 969 cm^{-1} was very unsatisfactory, and in our study of the concentration and temperature dependences only the band at 956 and a band resulting from the superposition of the bands at 965 and 969 cm^{-1}, designated as 967 cm^{-1}, were therefore considered. Based on the above-mentioned assignment of bands in the range 950–980 cm^{-1} to associates of various sizes, the change in the degree of association was characterized by the absorbance ratio of the bands at 956 and 967 cm^{-1} (E_{956}/E_{967}). The decrease of this ratio in Fig. 4 indicates alkoxide disaggregation with increasing temperature or decreasing solution concentration.

Adduct Stoichiometry

From the proved t-BuONa tetramer formation and the simultaneous decrease in the contents of higher associates in the presence of THF, it is evident that the adduct is the solvated tetramer – (t-BuONa)$_4$.n THF. The stoichiometry of the adduct, i.e. the "solvation" number n, corresponding to the number of THF molecules solvating the tetramer, was determined from the plot of the concentration of bound THF vs the alkoxide tetramer concentration. To this end the corresponding equilibrium concentrations were determined for a series of samples covering a broad concentration range of the components t-BuONa and THF in cyclohexane or heptane solution,
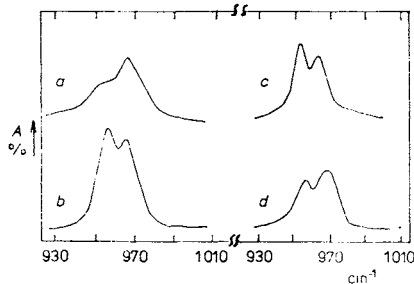

Fig. 3

Infrared spectra of cyclohexane solutions of t-BuONa in dependence on concentration c and temperature T: a $c = 0.010$ mol l^{-1}, $T = +25°C$; b $c = 0.850$ mol l^{-1}, $T = +25°C$; c $c = 0.164$ mol l^{-1}, $T = -21°C$; d $c = 0.164$ mol l^{-1}, $T = +55°C$
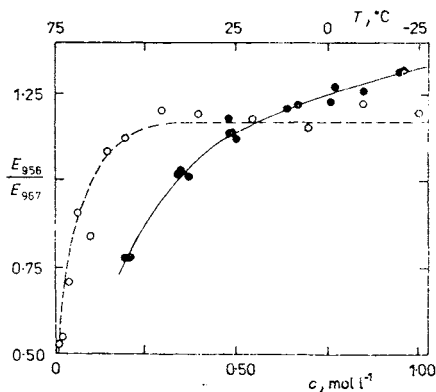

Fig. 4

Dependence of alkoxide disaggregation (characterized by the ratio E_{956}/E_{967}) on temperature and t-BuONa concentration - - - - concentration dependence (○), ——— temperature dependence (●)

in equimolar mixture, or with excess of one or the other component. The "solvation" number n was determined as equal to the slope of the plot: $n = 3 \cdot 14$. It is evident from Fig. 5 showing an analogous plot of the absorbance values of the corresponding bands E_{1057}/d vs E_{978}/d (d is the cell thickness) that the value of n is equal in both solvents. These results indicate that under the given conditions the tetramer in solution is solvated by three THF molecules on the average. At high THF excess with respect to t-BuONa (12 : 1 or 15 : 1), deviations from linearity may be observed in Fig. 5, corresponding to an increase in the "solvation" number. Evidently further solvation of the partly solvated alkoxide tetramers occurs, probably with the formation of a fully solvated tetramer, with $n = 4$.

Studies of the system with a large excess of THF revealed that the tetramer content as characterized by the band at 978 cm^{-1} increases up to about a seven fold excess of THF, at an alkoxide concentration $c_{BO} = 0 \cdot 120$ mol l^{-1} (see Fig. 6); this THF concentration evidently is necessary for complete t-BuONa transformation to the tetrametric form.

The drop of the curve at high THF concentrations is connected with a change in the absorbance coefficient due to a change in medium[10]. The total area of the bands in the range $950 - 970$ cm^{-1} corresponding to the concentration of higher associates ($x > 4$) approaches zero with increasing THF excess. Thus at sufficient THF excess the solution contains predominantly the alkoxide tetramer, which is solvated by four THF molecules at most.
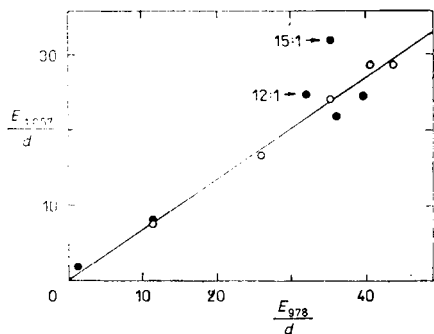

FIG. 5

Dependence of E_{1057}/d on E_{978}/d for solutions of THF + t-BuONa in cyclohexane (●) and heptane (○). Mole ratio THF : t-BuONa $= 1 : 3 - 10 : 1$, $12 : 1$, $15 : 1$; d is the cell thickness
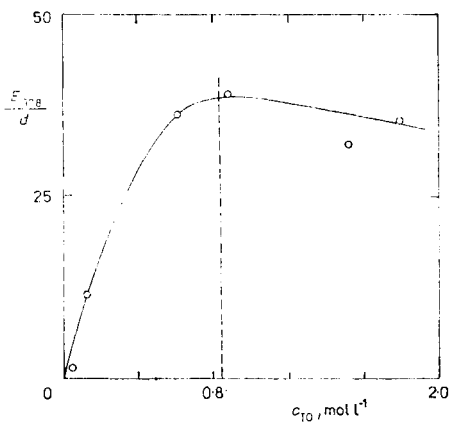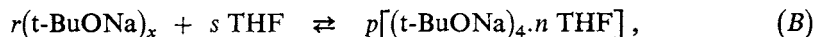
FIG. 6

Dependence of the equilibrium value of E_{978}/d for the t-BuONa band on the initial THF concentration in hydrocarbon solutions of the mixture of THF with t-BuONa. $c_{BO} = 0 \cdot 120$ mol l^{-1}

Stability Constant of the t-BuONa–THF *Adduct*

For calculation of the equilibrium constant, a quite general reaction scheme is proposed

$$r(\text{t-BuONa})_x + s\,\text{THF} \rightleftharpoons p[(\text{t-BuONa})_4 . n\,\text{THF}] , \qquad (B)$$

where x designates the degree of t-BuONa association.

This calculation was performed in a way independent of the "solvation" number determination from the concentration dependences. The only assumption employed here was the existence of the t-BuONa tetramer in the adduct. The other parameters were considered as unknown, and related as follows: $r \cdot x = 4p$, $s = p \cdot n$. By substitution for r in Eq. (B) and rearrangement, the basic equilibrium equation was obtained

$$4(\text{t-BuONa})_x + nx\,\text{THF} \overset{K'}{\rightleftharpoons} x[(\text{t-BuONa})_4 . n\,\text{THF}] \qquad (C)$$
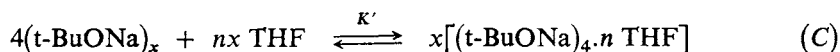
The equilibrium constant K' is defined by the relation

$$K' = c_A^x / (c_{TF}^{nx} \cdot c_x^4) , \qquad (1)$$

where c_A, c_{TF} and c_x are concentrations of the adduct $\{(\text{t-BuONa})_4 . n\,\text{THF}\}$, the free THF and x-mer of t-BuONa, respectively. With the experimentally determinable concentrations equation (3) for the equilibrium constant was obtained by introducing of the simplifying relations $(2a-c)$

$$c_A = c_{TAD}/n \qquad (2a)$$

$$c_{BO} = xc_x + 4c_A , \qquad (2b)$$

$$c_x = \left(c_{BO} - \frac{4}{n}c_{TAD}\right)\Big/ x \qquad (2c)$$

$$K' = c_{TAD}^x (nx)^4 / \{c_{TF}^{nx} n^x (nc_{BO} - 4c_{TAD})^4\} , \qquad (3)$$

where c_{TAD} is the concentration of THF bound in the adduct, c_{BO} is the initial concentration of t-BuONa. This expression contains only three unknowns: the degree of association x, the "solvation" number n, and the stability constant K'.

Equation (3) was solved logarithmically[10]. Based on a statistical evaluation of a set of experimental points corresponding to initial concentrations of t-BuONa in the range $c_{BO} = 0.05-0.95\,\text{mol}\,l^{-1}$, and of THF in the range $c_{TF} + c_{TAD} = 0.085-1.25\,\text{mol}\,l^{-1}$, the equilibrium constant and one more unknown were determined for a selected value of the third unknown. In this way the following values were found, characterizing the system THF with t-BuONa in cyclohexane in the above concentration range: $n = 3.0$, $x = 5.7$, $K' = 9.2 . 10^{11}$. The equilibrium

constant K' is defined by Eq. (1). The stability of the adduct should, however, be characterized by the strength of one —O—$[Na—O{<}]$ bond. The stability constant referred to one Na—O bond is equal to $K = K'^{1/(nx)} = 5{\cdot}01$. This value indicates that the adduct is of intermediate strength, comparable to some acceptor–donor adducts, e.g. I—C≡N + 1,4-dioxane, trinitrobenzene + N-tert. butyl aniline, chloroanil + 1,2 benzanthracene, where the equilibrium constants are $1{\cdot}2$, $5{\cdot}5$ and $5{\cdot}8$, respectively[14].

The found n value is in very good agreement with the value $3{\cdot}14$ determined from IR spectra by means of graphical analysis of the plot of bound THF vs tetramer concentration.

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