On the Mechanism of *n*-Butyl Vinyl Sulfide Formation with [K(18-crown-6)SBu] as Catalyst

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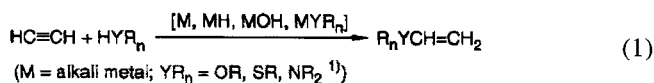Halle, Department of Inorganic Chemistry of the Martin-Luther-University

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Abstract. *n*-Butyl mercaptane reacts with acetylene in the presence of [K(18-cr-6)SBu] as catalyst to give *n*-butyl vinyl sulfide. In toluene the reaction is of zeroth order with respect to BuSH and first order with respect to [K(18-cr-6)SBu]. The reaction rate depends on the solvent in the following order: toluene > triglyme $\approx$ BuSH $\approx$ dioxane >> BuOH. In toluene, BuOH added in equimolar amounts accelerates the reaction indicating a complex formation [K(18-cr-6)(BuOH)SBu] with a higher catalytic activity. [K(18-cr-6)SBu] is monomeric in the solid state with d(K–S) = 3.051(2) Å. Potassium is displaced out of the mean plane defined by the six oxygen atoms of the crown ether by 0.626(3) Å. [K(18-cr-6)SBu] is a strong electrolyte in alcohols but practically no electrolytic dissociation takes place in solvents with low dielectric constants such as toluene and *n*-butyl mercaptane. From the results a reaction mechanism is derived with the addition of non-dissociated [K(18-cr-6)SBu] to acetylene as the rate-determining step.
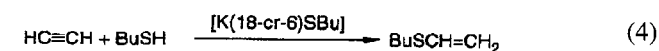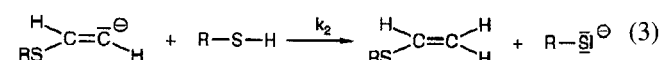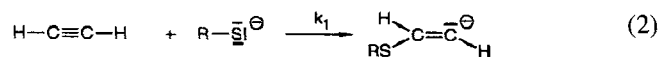
Nucleophilic additions to acetylene to give functionalized vinyl compounds [1] are catalyzed by bases according to the classical work of Reppe (eq 1) [2].

$$HC\equiv CH + HYR_n \xrightarrow{\text{[M, MH, MOH, MYR}_n\text{]}} R_nYCH=CH_2 \qquad (1)$$

(M = alkali metal; YR_n = OR, SR, NR_2 [1])

Furthermore, KOH/DMSO as superbasic catalyst system [3], and phase transfer catalytic systems [4] were described. The addition reaction of methanol to phenylacetylene in the presence of KOMe shows a first-order dependence on phenyl acetylene and on catalyst [5]. From these kinetic investigations Reppe derived the mechanism of the base-catalyzed nucleophilic addition of alcohols to acetylene. An analog mechanism was concluded for the addition of mercaptanes to acetylenes, cf. eq. 2 and 3 [2, 6]. The rate determining step is the addition of the mercaptide to acetylene (eq. 2) followed by fast protonation of the vinyl carbanion to give the vinyl sulfide (eq. 3).

In continuation of our work on the addition of RSH to acetylenes with KSR/crown ethers as catalysts [7], we dealt with the mechanism of the addition of *n*-butyl mercaptane to acetylene catalyzed by KSBu/18-crown-6 in weakly polar solvents according to eq. 4.

$$H-C\equiv C-H + R-\overline{\underline{S}}|^{\ominus} \xrightarrow{k_1} \underset{RS}{\overset{H}{\diagdown}}C=\overline{\underline{C}}{\overset{\ominus}{\underset{H}{\diagup}}} \qquad (2)$$

$$\underset{RS}{\overset{H}{\diagdown}}C=\overline{\underline{C}}{\overset{\ominus}{\underset{H}{\diagup}}} + R-S-H \xrightarrow{k_2} \underset{RS}{\overset{H}{\diagdown}}C=C{\overset{H}{\underset{H}{\diagup}}} + R-\overline{\underline{S}}|^{\ominus} \qquad (3)$$

$$HC\equiv CH + BuSH \xrightarrow{\text{[K(18-cr-6)SBu]}} BuSCH=CH_2 \qquad (4)$$

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1) Abbreviations: R = alkyl, aryl, H; 18-cr-6 = crown ether 18-crown-6; Bu = n-C$_4$H$_9$; BuSVi = *n*-butyl vinyl sulfide.

Results and Discussion

Rate Law of the Addition Reaction

Eq. 5 was established to be the rate expression for the n-butyl vinyl sulfide formation according to eq 4.

$$r = k \cdot c_{BuSH}^{0} \cdot c_{cat} \cdot c_{HC \equiv CH} \qquad (5)$$

The zero-order dependence on BuSH was proved by measuring the concentration of BuSH and BuSVi in dependence on time at constant concentrations of catalyst and acetylene, cf. Fig. 1. The first-order dependence on [K(18-cr-6)SBu] as catalyst was obtained from the reaction rate of the vinylation reaction at various catalyst concentrations (c_{cat}) but at constant concentrations of acetylene in BuSH as solvent, cf. Fig. 2. The first-order dependence on acetylene was not established experimentally in the reaction according to eq. 4 but in the analogous addition reaction of BuSH to phenyl acetylene to give (Z)-2-(n-butylthio)vinylbenzene.
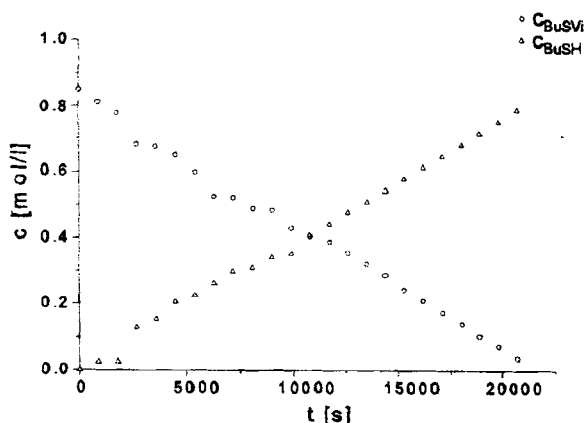
Fig. 1 Plot of c_{BuSH} and c_{BuSVi}, respectively, vs. t for the addition of BuSH to acetylene.Catalyst: [K(18-cr-6)SBu] (c_{cat} = 0.2082 mol/l); solvent: toluene; temperature: 30 °C.

Temperature Dependence

The second-order rate constants were experimentally determined in toluene between 30 and 70 °C, cf. Tab. 1. From the Arrhenius plot (Fig. 3) the activation energy E_A = (98 ± 3) kJ/mol and ln A = 32 ± 1 were derived. From the Eyring plot (Fig. 3) the activation enthalpy and entropy $\Delta H^{\neq}$ = (95 ± 3) kJ/mol and $\Delta S^{\neq}$ = (12 ± 10) J/(mol·K), respectively, were obtained. The slightly positive activation entropy could be caused by the participation of the non-dissociated ion pair [K(18-cr-6)SBu] in the rate-determining step.

Solvent Dependence

The dependence of the catalytic activity on solvent is shown in Tab. 2. In toluene the reaction proceeds 3–5 times faster than in etherial solvents (dioxane, triglyme)

and in n-butyl mercaptane. But in n-butyl alcohol the reaction rate decreases by about two powers of ten what may be caused by a relatively strong solvation of the catalyst via S–H–O bridges (cf. Gutmann's acceptor number AN(BuOH) = 33 [8]).
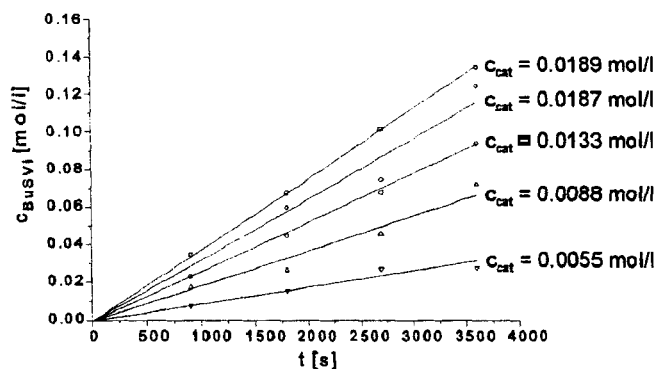
Fig. 2 Plot of c_{BuSVi} vs. t at various concentrations of [K(18-cr-6)SBu]. $c_{[K(18-cr-6)SBu]}$ = 0.0055 ... 0.0189 mol/l; solvent: BuSH; temperature: 70 °C.

The influence of alcohols on the analogous vinyl ether synthesis from acetylene and alcohols catalyzed by [K(18-cr-6)OR] is much more pronounced: In p-xylene as solvent the reaction rate is reduced so strongly already at a ratio $c_{ROH}/c_{[K(18-cr-6)OR]} \geq$ 1/1 that the reaction does not proceed at 70 °C [4].

Influence of n-Butyl Alcohol on Catalytic Activity

The influence of n-butyl alcohol on the activity of [K(18-cr-6)SBu] in toluene depends distinctively on the concentration of n-butyl alcohol as can be seen in Fig. 4. The maximum of catalytic activity at a ratio c_{BuOH}/c_{cat} = 1/1 indicates the formation of a complex [K(18-cr-6)(BuOH)SBu] with an enhanced nucleophilicity of mercaptide. The decreased catalytic activity at higher concentrations of n-butyl alcohol may be caused by the formation of S–H–O hydrogen bridges as described above.

Assuming that the complex stability is sufficient (thus, following in the range $c_{BuOH} \leq c_{cat}$ for the equilibrium

Table 1 Temperature dependence of rate constants of the vinylation reaction with [K(18-cr-6)SBu] as catalyst in toluene as solvent.

T °C	c_{cat} mol/l	$c_{HC \equiv CH}$ mol/l	r mol/(l·s)	k l/(mol·s)	sample numb. n
30	0.2082	0.1903	$4.57 \cdot 10^{-5}$	$1.1526 \cdot 10^{-3}$	10
40	0.2082	0.1555	$9.86 \cdot 10^{-5}$	$3.0440 \cdot 10^{-3}$	10
50	0.0209	0.1271	$2.94 \cdot 10^{-5}$	$1.1071 \cdot 10^{-2}$	9
60	0.0209	0.1039	$7.44 \cdot 10^{-5}$	$3.4287 \cdot 10^{-2}$	7
70	0.0209	0.0849	$1.77 \cdot 10^{-4}$	$9.9977 \cdot 10^{-2}$	6
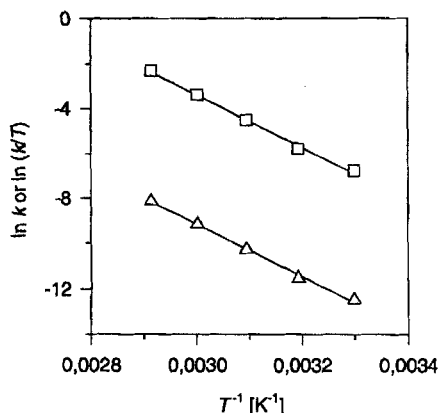
Fig. 3 Arrhenius (□) and Eyring (▲) plots of data for the n-butyl vinyl sulfide formation in toluene between 30 and 70 °C (correlation coefficients $r = 0.998$).

concentrations $c_{eq\,BuOH} \approx 0$, $c_{eq\,[K(18\text{-}cr\text{-}6)SBu]} \approx c_{cat} - c_{BuOH}$, $c_{eq\,[K(18\text{-}cr\text{-}6)(BuOH)SBu]} \approx c_{BuOH}$), eq. 6 follows for the overall reaction rate (r) which is the sum of the rates of two processes catalyzed by [K(18-cr-6)SBu] and [K(18-cr-6)(BuOH)SBu], respectively. r_{max} in Fig. 4 was calculated from eq. 6 demonstrating that the addition of one molecule n-butyl alcohol roughly doubles the activity of the catalyst.

$$r = k_{[K(18\text{-}cr\text{-}6)SBu]} \cdot c_{eq\,[K(18\text{-}cr\text{-}6)SBu]} \cdot c_{HC\equiv CH}$$

$$+ k_{[K(18\text{-}cr\text{-}6)(BuOH)SBu]} \cdot c_{eq\,[K(18\text{-}cr\text{-}6)(BuOH)SBu]} \cdot c_{HC\equiv CH}$$

$$= k_{[K(18\text{-}cr\text{-}6)SBu]} \cdot (c_{cat} - c_{BuOH}) \cdot c_{HC\equiv CH}$$

$$+ k_{[K(18\text{-}cr\text{-}6)(BuOH)SBu]} \cdot c_{BuOH} \cdot c_{HC\equiv CH} \qquad (6)$$

Influence of the Crown Ether on the Reaction Rate

Due to its unsolubility KSBu does not catalyze the formation of n-butyl vinyl sulfide in toluene, dioxane and n-butyl mercaptane at 70 °C. The rate constants in

triglyme and in n-butyl alcohol are given in Tab. 2. The [K(18-cr-6)SBu] catalyzed reactions are only slightly faster as can be seen from the relation of rate constants $k_{rel} = k_{[K(18\text{-}cr\text{-}6)SBu]}/k_{KSBu} = 1.20 \pm 0.19$ in triglyme and 1.48 ± 0.55 in n-butyl alcohol. The difference is significant $(p = 0.95)$ in triglyme but not in n-butyl alcohol.

From these investigations no conclusions can be drawn on k_{rel} in other solvents. Thus, the question can not be answered whether the high catalytic acitivity of [K(18-cr-6)SBu] in toluene is due to a „specific" effect of crown ether or is only due to the solubilization of KSBu by complex formation.

Molecular Structure of [K(18-cr-6)SBu]

The molecular structure of the precatalyst, [K(18-cr-6) SBu], is shown in Fig. 5. The compound is monomeric. There are no intermolecular contacts in the crystalline
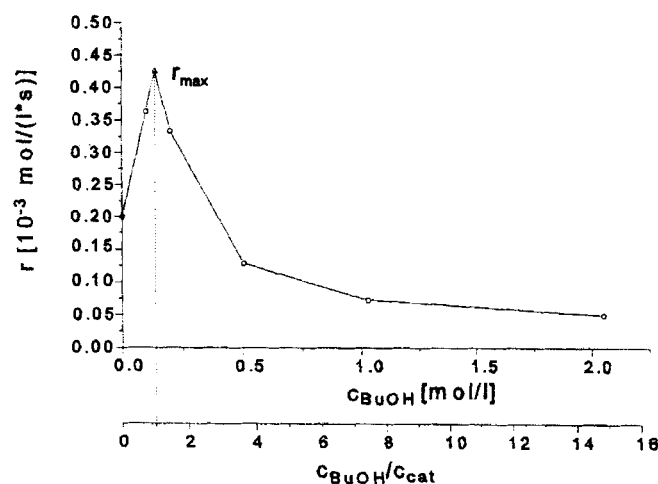

Fig. 4 Dependence of the reaction rate on the concentration of BuOH. Catalyst: [K(18-cr-6)SBu] $(c_{cat} = 0.1379$ mol/l); solvent: toluene; temperature: 50 °C.

Table 2 Dependence of the rate constants of addition of n-butyl mercaptane to acetylene with [K(18-cr-6-)SBu] or [KSBu] as catalyst on the solvent at 70 °C.

solvent	catalyst	c_{cat} mol/l	$c_{HC\equiv CH}$ mol/l	r mol/(l·s)	$k \pm$ conf. int.[a] l/(mol·s)
toluene	[K(18-cr-6)SBu]	0.0679	0.0849	$5.44 \cdot 10^{-4}$	0.0943 ± 0.0074
dioxane		0.0184	0.2350	$7.96 \cdot 10^{-5}$	0.0184 ± 0.0022
triglyme		0.0207	0.2641	$1.88 \cdot 10^{-4}$	0.0344 ± 0.0038
BuSH		0.0118	0.0773	$2.18 \cdot 10^{-5}$	0.0240 ± 0.0031
BuOH		0.0192	0.1050	$1.51 \cdot 10^{-6}$	0.0007 ± 0.0003
triglyme	[KSBu]	0.0383	0.2641	$2.89 \cdot 10^{-4}$	0.0286 ± 0.0036
BuOH		0.3572	0.1050	$1.90 \cdot 10^{-5}$	0.0005 ± 0.0001

[a] $p = 0.90$

state. Potassium has the C.N. 7 with six contacts to oxygen (mean value d(K–O): 2.853 Å) and one contact to sulfur. Potassium is displaced out of the mean plane defined by the six oxygen atoms of the crown ether by 0.626(3) Å. The distance d(K–S) amounts to 3.051(2) Å. This value is shorter than the K–S distances in [K(SR)(thf)]$_x$ (RS$^-$ = 2,4,6-tris(trifluormethyl) benzene-thiolate) (3.159(1) Å) with its triply bridging sulfur atoms (μ^3-SR) [9] and is nearly the same as the K–S
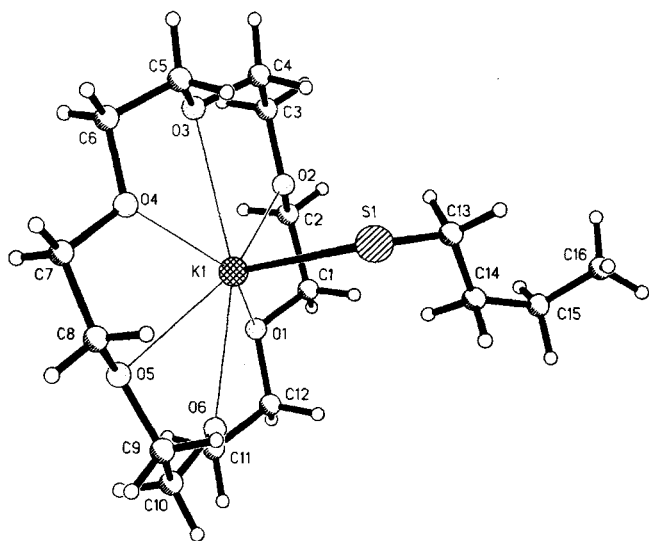
Fig. 5 Molecular structure of [K(18-cr-6)SBu]. Selected bond lengths (Å) and angles (°): K1–O 2.782(5) to 2.958(5) (mean: 2.853), C–O 1.403(9) to 1.426(8) (mean: 1.418), C–C 1.44(1) to 1.52(1) (mean: 1.49), K1–S1 3.051(2), S1–C13 1.81(1); C–O–C 111.1(6) to 114.8(6) (mean: 112.8), C–C–O 106.8(6) to 111.0(6) (mean: 108.8), K1–S1-C13 98.5(5)

distances in [K(18-cr-6)]$_2$S$_6$·2 MeCN (3.075(2) Å) [10]. Furthermore, d(K–S) in [K(18-cr-6)SBu] is also shorter than the sum of ionic radii of a K$^+$ and a S^{2-} ion (3.22 Å [11]).

Due to the head to head arrangement in the crystal and the large steric demand at the crown ethers, the extended *n*-butyl groups have a lot of space available and are disordered.

[K(18-cr-6)SBu] is the first structurally characterized potassium salt of a monodentate thiolate which is monomeric.

On the Electrolytic Dissociation of [K(18-cr-6)SBu]

From measurements of specific conductivities of [K(18-cr-6)SBu] solutions it was established that [K(18-cr-6)SBu] is a strong electrolyte in methanol and in *n*-butyl alcohol. But electrolytic dissociation according to eq. 7 practically does not take place in solvents with low dielectric constants such as toluene and *n*-butyl mercaptane (Tab. 3).

Table 3 Molar conductivities at zero concentration (Λ_0) and apparent dissociation constants (K') of [K(18-cr-6)SBu] in organic solvents. Gutmann's donor (DN) and acceptor numbers (AN) [8] and relative dielectric constants (ε) [15] are given for comparison.

solvent	Λ_0	K'_{diss} mol/l	DN	AN	ε
MeOH	82.2	$2 \cdot 10^{-2}$	20	41	32.6
BuOH	29.8	$1 \cdot 10^{-3}$	18	33 [b]	17.0
BuSH	152 [a]	$1 \cdot 10^{-10}$ [c]			5.1
toluene	129 [a]	$< 1 \cdot 10^{-11}$ [d]	0.1 [e]	8 [e]	2.4

[a] Calculated with Walden's rule from Λ_0(MeOH). [b] Value for propyl alcohol. [c] c = 1 mmol/l [d] c = 0.3 mmol/l [e] Value for benzene.

$$\text{[K(18-cr-6)SBu]} \rightleftharpoons \text{[K(18-cr-6)]}^+ + \text{BuS}^- \qquad (7)$$

Thus, in these weakly polar solvents [K(18-cr-6)SBu] has to be considered as the nucleophile which attacks on acetylene. If the anion BuS$^-$ would be the attacking nucleophile, then the reaction order should be 1/2 in [K(18-cr-6)SBu] due to the very low electrolytic dissociation of [K(18-cr-6)SBu] in these solvents (cf. Tab. 3). This is in contradiction to the experimental results

On the Mechanism of the Addition Reaction

From the investigations follows that the addition of mercaptanes to acetylene to give vinyl sulfides in weakly polar solvents like aromatic hydrocarbons presumably proceeds according to the catalytic cycle in Fig. 6. Three main steps of the reaction are discussed:

1. The rate determining step is the addition of the non-dissociated catalyst (**I** [2]) to acetylene to give **II**.
2. The negative partial charge arising at the vinyl-C atom is taken over by a mercaptane molecule from the nearest surroundings to give **III**.
3. Most likely simultaneously with the formation of the reaction product **IV**, the regeneration of **I** proceeds *via* addition of RSH to the [K(18-cr-6)] fragment which bears a positive partial charge. The proton released will be transferred – presumably with participation of other mercaptane molecules – to the RS moiety bearing a negative partial charge. It is most unlikely that free ions are involved in these processes.

Principally step **II** → **III** can also proceed with participation of acetylene. This will happen if there are no mercaptane or other protic substances in the reaction mixture. Then potassium acetylide – if the occasion arises as crown ether complex – is formed which presumably catalyses the formation of vinyl acetylene and poly-acetylene in an analogous cycle.

[2] **I** to **IV** refer to Fig 6
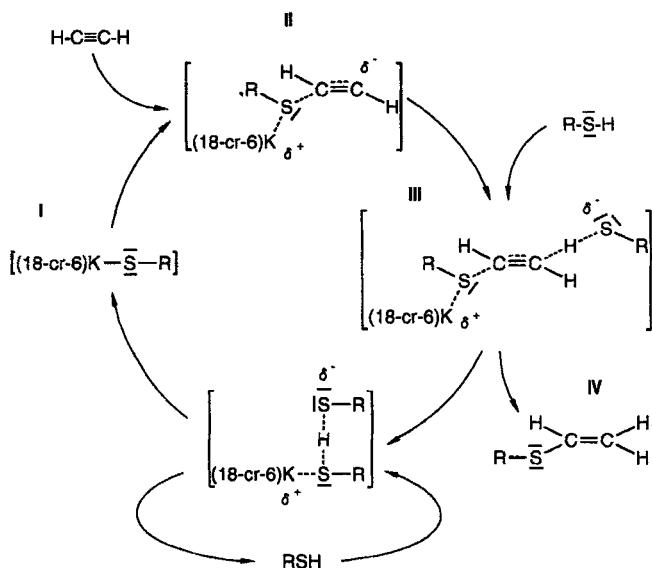
Fig. 6 Proposed catalytic cycle of mercaptane addition to acetylene with [K(18-cr-6)SR] as catalyst in weakly polar solvents.

If no proton donors are present in the reaction mixture, then the negative partial charge at the vinyl-C atom arising in **II** can be compensated by coordination to [K(18-cr-6)] to give 2-(alkylthio)vinyl potassium. Compounds like that are not described in literature. It can be expected that they are decomposed in an heterolytic fragmentation reaction to give the starting compounds already at very low temperatures (eq 8).

$$[K(18\text{-}cr\text{-}6)CH=CHSR] \quad \Longleftrightarrow \quad [K(18\text{-}cr\text{-}6)SR] + HC\equiv CH \tag{8}$$

An analogous reaction was described: LiCH=CHOR decomposes at –50 °C to give acetylene and LiOR [12].

Thus, it was established that the addition of mercaptanes to acetylene with [K(18-cr-6)SR] as catalysts in weakly polar solvents proceeds as rate determining re-addition of the non-dissociated ion pair [K(18-cr-6)SR] followed by fast protonation/deprotonation steps.

Experimental

Materials and General Procedures

General procedures were described under argon in lit. [7]. Toluene, mesitylene, dioxane and triglyme were distilled from sodium benzophenone ketyl and lithium aluminum hydride, respectively. Methanol, n-butyl alcohol and n-butyl mercaptane were dried over magnesium methoxide/butoxide and calcium chloride, respectively, and were distilled under argon. [KSBu] and [K(18-cr-6)SBu] were prepared as described in lit. [7].

Kinetics

A weighed amount of KSBu was given into a two-necked Schlenk tube (10 ml) with heating jacket, and a solution of 18-cr-6 (KSBu/18-cr-6 = 1.1/1), BuSH and mesitylene (used as internal reference for GC) in toluene was added by a Schlenk burette. The Schlenk tube was equipped with a reflux condenser and an inlet pipe through which argon was bubbled for 30 min at the reaction temperature. (The quantitative formation of [K(18-cr-6)SBu] under these conditions was checked in separate experiments by acidimetric titration of the filtered solution.) Then acetylene was passed through the reaction mixture (2–5 l/h). Probes were removed from the Schlenk tube at suitable time intervals (see Fig. 1) with a microliter syringe through a septum and analyzed by gas chromatography (6 m × 3 mm, 10 % SE 52 on chromaton N super; detector: FID). Mesitylene was used as internal standard, and calibration factors were determined twice immediately before and after the experiments by means of standard mixtures.

The reaction order with regard to PhC≡CH was determined in the reaction between PhC≡CH (c_0 = 0.3546 mol/l) and BuSH (c_0 = 0.9492 mol/l) in toluene at 40 °C ($c_{[K(18\text{-}cr\text{-}6)SBu]}$ = 0.0215 mol/l) and 60 °C ($c_{[K(18\text{-}cr\text{-}6)SBu]}$ = 0.0054 mol/l) by analyzing (GC) the decrease of $c_{PhC\equiv CH}$ in dependence on time ($t = 0$ .... 8400 s) and plotting $\lg c_{PhC\equiv CH}$ vs. t (regression coefficient r = 0.98 at 40 °C and r = 0.99 at 60 °C).

Determination of Acetylene Solubility in Toluene

A Schlenk tube equipped with an inlet pipe was filled with toluene and mesitylene as internal standard for GC and thermostatted (24 ... 70 °C). After passage of acetylene through the mixture for 10–20 min, probes were removed from the Schlenk tube with a microliter syringe through a septum, and the acetylene concentration was determined by gas chromatography (6 m × 3 mm, 10% SE 52 on chromaton N super; detector: FID). Calibration factors were determined by reference measurements in benzene at 25 °C $c_{HC\equiv CH}^{benzene}$ = 0.2313 mol/l [13]). From the data obtained, eq. 9 was derived for the temperature dependence of acetylene concentration.

$$\ln c_{HC\equiv CH}^{toluene} = -1.5582 - 0.02018 \, K^{-1} \cdot (T - 298.15 \, K) \tag{9}$$

The parameters were obtained by linear regression. The confidence interval (p = 0.90) for the mean values of $\ln c_{HC\equiv CH}^{toluene}$ is ±0.0509.

X-Ray Structure Determination of [K(18-cr-6)SBu]

The data were collected on a STOE-STADI4 diffractometer at 220 K using Mo-K_α radiation. All calculations were performed using SHELXL-93. Crystal dimensions 0.4 × 0.2 × 0.2 mm. Elementary cell (monoclinic) a = 13.535(3) Å, b = 18.292(4) Å, c = 8.540(2) Å, β = 97.73°. Cell volume V = 2095.2(8) Å³. Formula units/elementary cell Z = 4. Space group

Cc. Further details of the crystal structure investigation are available on request from the FIZ Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CDS 404036, the names of the authors, and the journal citation.

Measurement of Specific Conductivities

In a two-necked Schlenk tube equipped with the measuring cell (conductometer: LF 537; cell LR 01/T from WTW), a Schlenk burette and a magnetic stirrer, the specific conductivity of 100.0 ml solvent (MeOH, BuOH, BuSH) was measured at 25.0 ± 0.1 °C (κ_o). Then via a Schlenk burette a stock solution of [K(18-cr-6)SBu] in the solvent was added gradually and the specific conductivities (κ) were measured. The molar conductivities Λ were obtained by the relationship $\Lambda = (\kappa - \kappa_o)/c$. The apparent dissociation constants K' and the molar conductivities at zero concentration Λ_o were calculated from the linearized form of Ostwald's dilution law $K' = \Lambda^2 c/\Lambda_o (\Lambda_o - \Lambda)$.

MeOH: $c_{[K(18-cr-6)SBu]} = 0.23 - 5.05$ mmol/l; $\kappa = 0.44 - 0.38$ µS/cm; $\Lambda = 81.99 - 69.40$ S cm²/mol; number of datapoints $n = 16$; coefficient of regression $r = 0.98$.

BuOH: $c_{[K(18-cr-6)SBu]} = 0.15 - 0.94$ mmol/l; $\kappa = 4.2 - 18.4$ µS/cm; $\Lambda = 27.25 - 19.45$ S cm²/mol; $n = 13$; $r = 0.94$.

Specific conductivities $\Lambda = 0.02 - 0.11$: µS/cm ($n = 6$) and $\Lambda < 6$ nS/cm were measured in BuSH as solvent ($c_{[K(18-cr-6)SBu]} = 0.41 - 2.06$ mmol/l) and in saturated solution of [K(18-cr-6)SBu] in toluene ($c_{[K(18-cr-6)SBu]} = 0.323$ mmol/l), respectively. Due to the very low conductivities the zero concentrations Λ_o were estimated from Walden's rule (viscosity coefficients taken from lit. [14] and the apparent dissociation constants K' were calculated from Ostwald's law at $c = 1$ mmol/l and $c = 0.3$ mmol/l, respectively.

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