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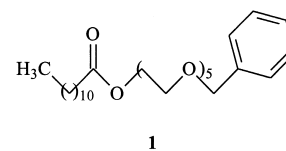
Fatty Acid-Oligo(ethylene glycol) Ester Forms Ion Channels in Lipid Membranes**

Tanja Renkes, Hans J. Schäfer,* Peter M. Siemens, and Eberhard Neumann*

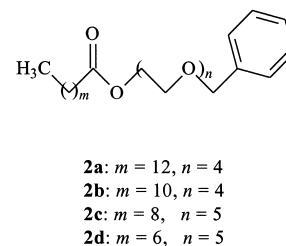
In memory of Eberhard Steckhan

Alkali and alkaline-earth ions can be selectively transported through biological cell membranes by proteins which form ion channels. The passage of ions through these channels can be controlled either by an electrical potential difference or by transmitter molecules.^[1, 2] In spite of extensive knowledge on the biophysics of ion conductivity across membranes, the detailed mechanism of transport on the molecular level is still not clear.^[2, 3] Since there is only limited access to chemical structures of natural ion channels, either through X-ray structure analysis or NMR spectroscopy,^[4] one may identify structural elements by the synthesis and characterization of artificial ion-channel forming compounds.^[5] Besides models with peptides as the main structural element, different nonpeptidic structures have been described as ion-channel forming compounds.^[6, 7] Of special interest in this connection is **1**, prepared by Menger.^[8] Compound **1** is reported to form proton channels by spanning, in a stretched form, the whole length of the lipid membrane. The spontaneous incorporation

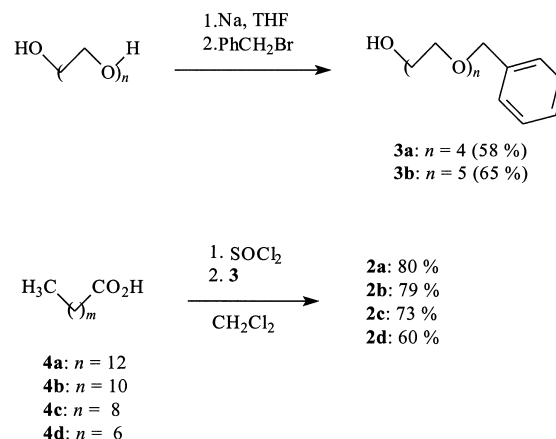
of **1** in lipid membranes is caused by both the hydrophobic section of the fatty acid chain and by the cationic π -interaction of the benzyl group with the choline group of the lipid. When embedded in the membrane, the oligo(ethylene glycol) chain can cause a localized increase in hydrophilicity of the membrane.^[9]



Here, we report the synthesis and characterization of the channel forming compounds **2a–d**, which are structurally similar to **1** but vary in the length of the fatty acid and the oligo(ethylene glycol). The activity of the channels has been analysed by fluorescence spectroscopy and, for the first time, by the electrical conductivity of single channels.



The channel-forming compounds **2a–d** are obtained in two steps. First, tetra- and pentaethylene glycol are converted by a Williamson ether synthesis into the corresponding monobenzyl ether **3a** and **3b**. These are then esterified with fatty acids **4a–d** to form **2a–d** (Scheme 1).



Scheme 1. Preparation of the channel-forming compounds **2a–d**.

In order to examine their activity as channel-forming compounds the esters **2a–d**, compound **1** and gramicidin D were integrated into lipid vesicles consisting of 1,2-dipalmitoyl-*sn*-glycero-3-phosphatidylcholin (DPPC). The rate of the ionic flux through the vesicle membrane was determined by time-resolved fluorescence spectroscopy, in which pyranine served as a pH indicator. When excited at 450 nm, pyranine exhibits a maximum in the emission spectrum at 511 nm for pH values above 7.2; this intensity maximum strongly decreases at pH values below 7.2.^[10] The DPPC vesicles were prepared and suspended in a weakly buffered pyranine solution (pH 7.7).^[11] Pyranine outside the vesicles was then removed by two passes through a gel filtration unit, such that the fluorescence of the probe is exclusively due to the pyranine inside the vesicles and it can therefore be used as a measure of the proton concentration. Decreasing the pH value

[*] Prof. Dr. H. J. Schäfer, Dipl.-Chem. T. Renkes
 Institut für Organische Chemie der Universität Münster
 Corrensstrasse 40, 48149 Münster (Germany)
 Fax: (+49) 251-8339772
 E-mail: schafeh@uni-muenster.de

Prof. Dr. E. Neumann, Dipl.-Chem. P. M. Siemens
 Physikalische und Biophysikalische Chemie
 Fakultät für Chemie
 Universität Bielefeld
 Postfach 10 01 31, 33501 Bielefeld (Germany)
 Fax: (+49) 521-1062981
 E-mail: eberhard.neumann@uni-bielefeld.de

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outside the vesicles by only one unit leads to a fluorescence decay in the presence of an ion-channel forming compound.^[12] This decay can be separated into two different phases. The initially rapid decrease results from an electrically uncompensated diffusion of protons into the vesicle, which creates a transmembrane potential difference. This potential difference induces a slow diffusion of K^+ ions to the outside and thereby allows further proton transport into the vesicle. Under these conditions, the fatty acid ester pores apparently conduct protons as well as K^+ ions.^[12]

Figure 1 shows that **2a–d** form ion channels which differ in the degree of the promoted ion flux. A comparison shows that **2a** and **2d** transport protons and K^+ ions less efficiently than **1**; **2b** and **2c** exhibits a slight and significantly better ion-channel activity, respectively, than **1**.^[13] These different trans-

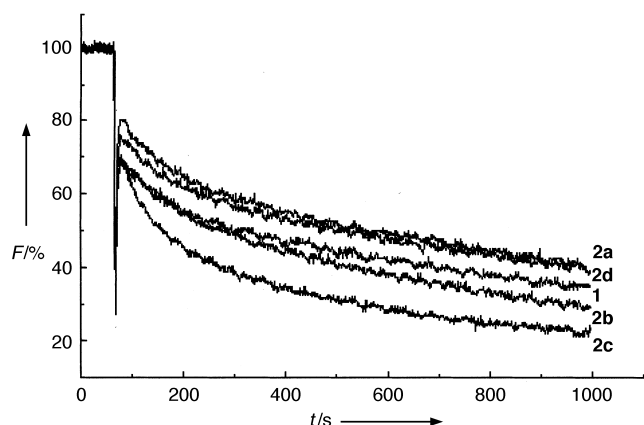


Figure 1. Fluorescence emission ($\lambda(\text{ex})=450$, $\lambda(\text{em})=511$ nm) of the vesicle suspension that contains pyranine (from 0.2 g L^{-1} (0.2 mM) DPPC, $d=100$ nm) in phosphate buffer (pH 7.7), which contains **1** or **2a–d** at a concentration of $4 \times 10^{-3} \text{ g L}^{-1}$ (about $8 \text{ }\mu\text{M}$). At a time $t=65$ s, the pH value was reduced from 7.7 to 6.7.

port properties permit some conclusions to be made on the relationship between structure and activity of the channel-forming compounds. If two compounds, like **1** and **2b** or **2a** and **2c**, are consistent in length and sufficiently hydrophobic to be incorporated into the membrane, the compound containing more oxygen atoms shows higher ion-channel activity. The length of the channel-forming compound exhibits an optimum, illustrated by the comparison of **2c** with **1** or **2a** with **2b**. The most favorable ratio between the total chain length and the number of ethylene glycol units occurs in **2c**, which exhibits the highest channel activity. In spite of the same number of ethylene glycol units, **2d** has a substantially lower ion-channel activity than **2c**. Therefore, it is assumed that the hydrophobic portion in **2d** is too small and the length too short for an ideal integration into the membrane.

Further conclusions that concern the structure of the ion channels composed of **2a–d** can be drawn when comparing **2c** with the natural ion channel-forming compound gramicidin D (Figure 2). In contrast to **2c**, gramicidin D can significantly increase the proton concentration inside the vesicle at a concentration of only $2 \times 10^{-3} \text{ g L}^{-1}$ ($1 \text{ }\mu\text{M}$). However, a further increase of the concentration of gramicidin D, to $5 \text{ }\mu\text{M}$, barely

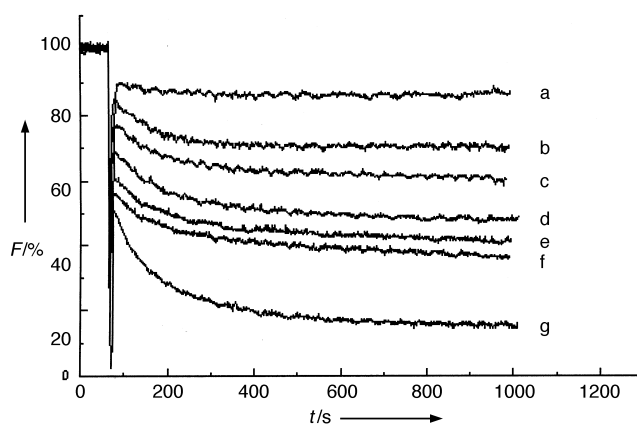


Figure 2. Fluorescence emission of pyranine in vesicles without (a) and with added gramicidin D (d: $2 \times 10^{-3} \text{ g L}^{-1}$ ($1 \text{ }\mu\text{M}$); e: $4 \times 10^{-3} \text{ g L}^{-1}$ ($2 \text{ }\mu\text{M}$); f: $1 \times 10^{-2} \text{ g L}^{-1}$ ($5 \text{ }\mu\text{M}$)) or **2c** (b: $2 \times 10^{-3} \text{ g L}^{-1}$ ($4 \text{ }\mu\text{M}$); c: $4 \times 10^{-3} \text{ g L}^{-1}$ ($8 \text{ }\mu\text{M}$); g: $1 \times 10^{-2} \text{ g L}^{-1}$ ($20 \text{ }\mu\text{M}$)) to a phosphate buffer (pH 7.7), experimental conditions are as in Figure 1.

improves the ion conductivity, which indicates a limiting value of its ion-channel activity. Raising the concentration of **2c** to $20 \text{ }\mu\text{M}$, however, leads to a further increase in the ion channel-activity. Finally, the effectiveness of the channels formed by **2c** is higher than that of channels consisting of gramicidin D. This observation indicates that **2c** does not form channels with less activity than gramicidin D but it needs, in contrast to gramicidin D, more than two molecules to assemble an ion channel.^[14] With respect to pore formation, the hydrophilic part of the ion-channel forming compound must span the whole membrane. Therefore, we assume that the molecules are oriented head-to-tail.

Whereas fluorescence emission spectroscopy reflects a continuous superposition of many channel events, electrical measurements provide information on the conductance and the dynamics of a single channel event.^[15] A soybean lipid with 20% phosphatidyl choline/cholesterol (9/1, w/w) was shown to be suitable as the planar membrane matrix.^[16] Typical channel activities, at a transmembrane potential difference of $+100$ mV in the presence of 1 M KCl as supporting electrolyte, are presented in Figure 3. Under these conditions, **1** shows no channel activity and **2b** shows only a decrease of the membrane resistance but no single channel events.

In contrast, **2a**, **2c**, and **2d** clearly exhibit single channel events (Figure 3). In order to show that the ion channels formed by **2** specifically transport cations, further experiments with **2** and LiCl (Figure 4) or CsCl (Figure 5) were carried out. As before, only **2a**, **2c**, and **2d** show single channel events. The single channel currents of **2a**, as well as those of **2c** and **2d**, are significantly higher in the presence of Cs^+ ions and much lower in the presence of Li^+ , as compared to KCl, as the supporting electrolyte.

The increase of the single channel currents from Li^+ through K^+ to Cs^+ correlates with the increase of the ion radii (Li^+ 78, K^+ 133, Cs^+ 169 pm),^[17] as well as with the decrease of the radius of the hydrated ions (Li^+ 382, K^+ 331 pm, Cs^+ 329 pm).^[17] Therefore, the cations passing through the channels have to strip off their hydration layer, at least partially. Hence, the pore diameter of such an ion channel must lie between 340 pm and 660 pm.

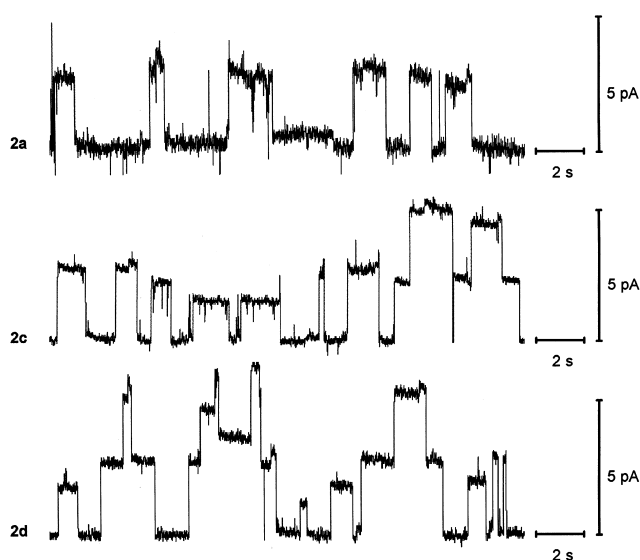


Figure 3. Single channel events (channels) of **2a**, **2c**, and **2d** in planar lipid bilayer membranes at a transmembrane voltage of $U = +100$ mV, current–time tracks (I/pA ; t/s) for 20 s. Experimental conditions: membrane: soybean lipid extract with 20 % phosphatidyl choline/cholesterol (9/1, w/w) and $2.5 \mu\text{M}$ **2a**, **2c**, or **2d** in the buffer; buffer: 1 M KCl; 296 K; filter frequency: 100 Hz; sample rate: 500 Hz.

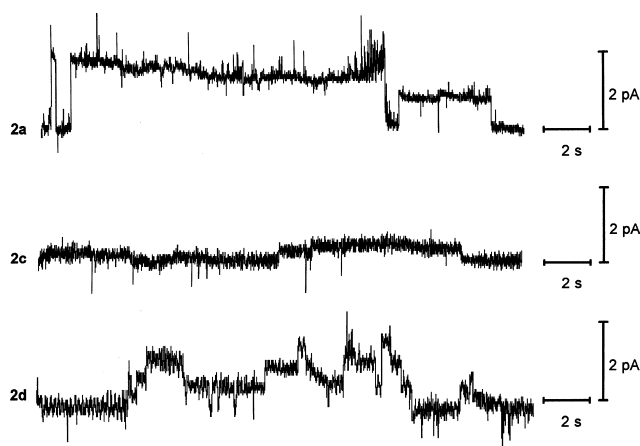


Figure 4. Single channel events (channels) of **2a**, **2c**, and **2d** in planar lipid bilayer membranes at a transmembrane voltage of $U = +100$ mV and buffer 1 M LiCl; all other conditions are as in Figure 3.

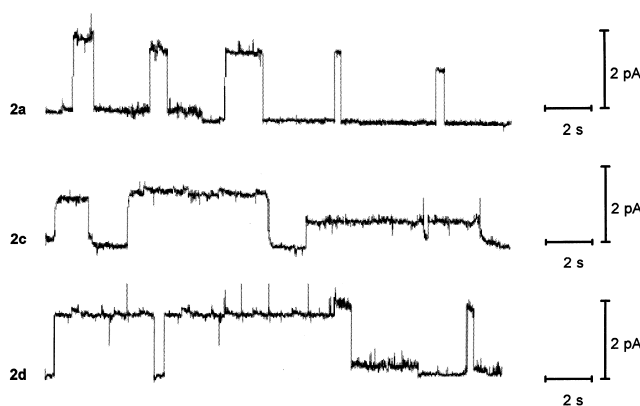


Figure 5. Single channel events (channels) of **2a**, **2c**, or **2d** in planar lipid bilayer membranes at a transmembrane voltage of $U = +100$ mV and buffer 1 M CsCl; all other conditions are as in Figure 3.

At the same membrane potentials, **2c** and **2d** show several single channel events that differ in their current intensity (Figure 6). In contrast, the single channel currents of **2a** exhibit only one distinct single channel current value (Figure 6) and the current–voltage dependence is linear with a conductance of 26 ± 1.5 pS (Figure 7).

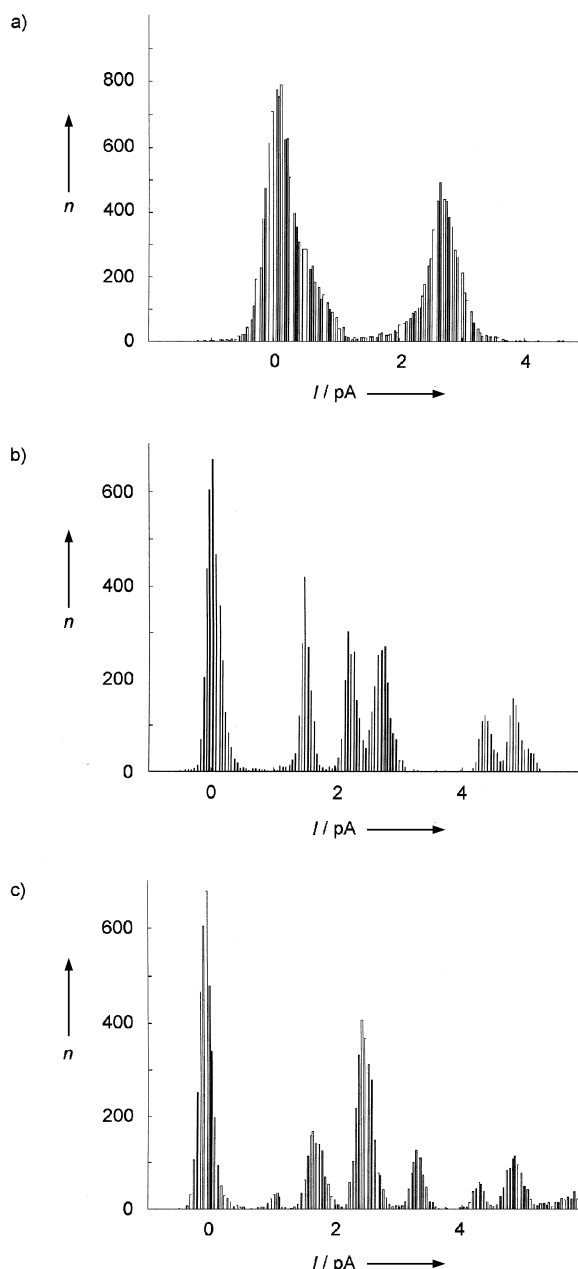


Figure 6. Amplitude histogram of the channel tracks from Figure 3 (**2a** (a), **2c** (b), and **2d** (c)) representing the frequency of the channel currents n as a function of the current (I/pA). Experimental conditions are as in Figure 3.

Apparently, the ion channels formed by the fatty acid esters differ in their constitutions. Pores formed by **2a** consist of a uniform diameter, whereas **2c** and **2d** can assemble to pores with different diameters. This difference is probably due to a variable number of molecules which form the ion channels.

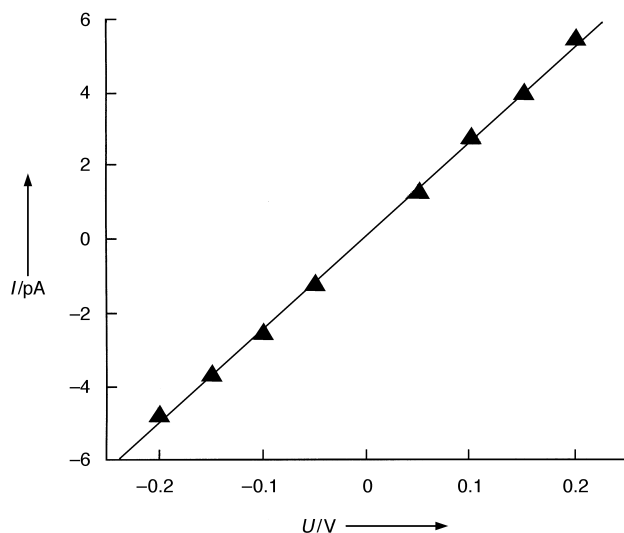


Figure 7. Symmetrical potential dependence of the single channel current of **2a**; linear regression leads to a conductance of $G = 26 \pm 1.5$ pS. Experimental conditions: membrane: soybean lipid extract with 20% phosphatidyl choline/cholesterol (9/1, w/w) and $2.5 \mu\text{M}$ **2a** in the buffer; buffer: 1M KCl; 296 K; filter frequency: 100 Hz; sample rate: 500 Hz.

In summary, based on the motif of **1**, new compounds have been prepared and identified as ion channels. They have several advantages compared to other artificial channel-forming compounds: They most probably span the membrane, their synthesis is fairly simple, and their structure provides the possibility to vary the head group, the number of the ethylene glycol units, or the ratio of the hydrophilic to hydrophobic part of the chain. The conducting pores are shown to consist of several molecules of the respective ion channel-forming compound; they require no rigid elements for ion conductivity.

Experimental Section

A) Synthesis of 2 and 3: The purity (>99%) and structure of all new compounds have been determined by gas chromatography, ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis or high resolution mass spectrometry.

3: The appropriate ethylene glycol (1 equiv) was slowly added with stirring and reflux under argon to a suspension of sodium in water-free THF (5 mL) until the sodium was totally dissolved. To this solution at 296 K, benzylbromide (1 equiv) was added and subsequently refluxed for 5 h. Water (10 mL) was then added, the aqueous phase extracted with ethyl acetate (3×5 mL), the combined organic phases dried over MgSO_4 , and the solvent removed by rotary evaporation. Flash chromatography with ethyl acetate provided the product as colorless oil.

2: To **4a–d** (1.25 equiv) in water-free dichloromethane (10 mL) under argon, a slight excess of thionyl chloride was added and the solution refluxed until gas evolution stopped. The solvent and excessive thionyl chloride were removed under vacuum. Thereupon the acid chloride was cautiously added, with ice-water cooling, to a solution of **3a** or **3b** (1 equiv) in water-free dichloromethane (10 mL) and triethylamine (1 mL) and was then stirred for 24 h at 296 K. Water (10 mL) was added to this solution and the mixture neutralized with dilute HCl. The aqueous phase was extracted with ethyl acetate (3×15 mL). The combined organic phases were dried over MgSO_4 , the solvent removed under vacuum, and the product purified by flash chromatography.

B) Fluorescence emission of pyranine-containing vesicles: The vesicles were prepared from DPPC (1 mg) and phosphate buffer (pH 7.7, 293 K) containing 0.1M KCl and 5×10^{-4} M pyranine.^[11] Pyranine outside the

vesicles was removed by two passes through a gel filtration unit (Sephadex G-25) with a phosphate buffer (pH 7.7, 0.1M KCl) as eluent. For the fluorescence measurements (Digital Spectrofluorophotometer R-510, Shimadzu), 200 μL of this solution was diluted with the same phosphate buffer to 1 mL. Thereupon, 2–10 μL of a solution of **1**, **2a–d**, or gramicidin D in methanol are added and stirred for 5 min. (which corresponds in the vesicle solution to 2×10^{-3} – 1×10^{-2} g L $^{-1}$ —approximately 4–20 μM **1** and **2a–d**, respectively, and 1–5 μM gramicidin D). Thereafter, by addition of HCl the pH value outside the vesicle was lowered to 6.7 and the decrease of the fluorescence was measured. Light scattering experiments show that the DPPC vesicles are not dissolved by concentrations up to 30 mol-% of **1** or **2a–d**, which is higher than the concentrations used for the fluorescence and the conductivity measurements. Additionally at room temperature, the critical micelle concentration of **2c** was determined, from the concentration dependence of the surface tension, to be 1.4×10^{-2} g L $^{-1}$.

C) Single channel events of the channel-forming compounds in planar lipid membranes: The planar lipid membranes are prepared using the monolayer-folding technique.^[18] For that purpose, in each of the compartments of the cell, saline solution (0.7 mL, sterile filtered 1M KCl, LiCl, or CsCl, $T = 296$ K) was added. On top of the buffer, a lipid solution (10 μL , soybean lipid extract with 20% phosphatidyl choline/cholesterol (9/1, w/w; Avanti Polar Lipids Inc., Alabaster, USA), 4 mg mL $^{-1}$ in *n*-pentane) was added. After waiting 10 min, when the pentane had evaporated, a planar lipid membrane with a diameter of about 100 μm spontaneously formed across the hole in the teflon septum by raising and lowering the liquid level in the cell.

To both compartments of the cell, the channel-forming compounds are added as 0.5 mm solutions in ethanol. The final concentrations were 2.5–5 μM . About 2–3 min after addition of the compounds, the first single channel events were observed.

In all experiments, the sign of the potential difference refers to the side of the membrane which is connected through the Ag/AgCl electrode to the voltage supply. This side is called the *cis* side, the other the *trans* side. A positive current corresponds to a cation transfer from the *cis* to the *trans* side and is registered in the corresponding figures as an upward signal.

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Aluminum Fluoride as a Storage Matrix for Atomic Hydrogen **

Gudrun Scholz,* Reinhard Stoer, Jan Alam Momand, Andrea Zehl, and Jeannette Klein

Atomic hydrogen H• can be stabilized for years in a suitably prepared AlF₃ powder matrix at temperatures $T \geq 300$ K (Figure 1). The hydrogen atoms are formed within the matrix by γ irradiation, essential OH groups in the crystallites serve as precursors for the H•. Thus, for the first time the stabilization of the reactive H• atoms has been achieved in a fluoride of the earth metals. A prerequisite for the formation and stabilization of the H• atoms is a special preparation of AlF₃ under quasi isobaric conditions,^[1] in which, in chemically and thermally controlled reactions of α - and β -trihydrates of AlF₃,

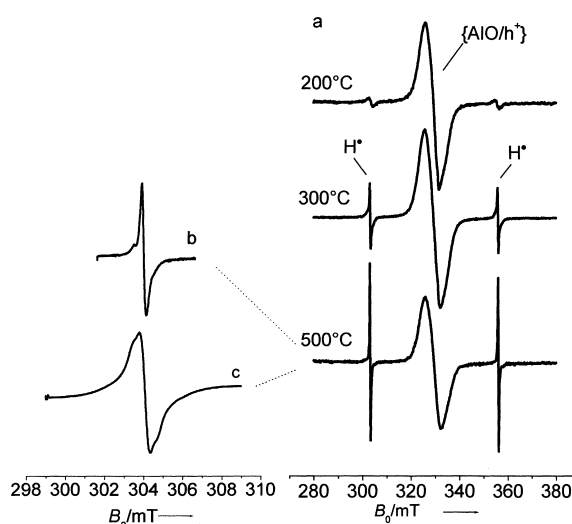


Figure 1. X-band ESR spectra (298 K) of trapped H• atoms: a) in AlF₃ powder samples of increasing crystallinity prepared from β -AlF₃·3H₂O under quasi isobaric conditions^[1] at the temperatures given. b, c) Low-field signal of the trapped H• atoms in AlF₃, prepared by annealing of β -AlF₃·3H₂O at 500 °C (P_{MW} = 2 mW), measurement temperature 298 K (b), 4.2 K (c); the y axis scales are identical.

both the necessary cage-like structural elements and also the H• precursors are formed. Parallel to the long-term stability of the enclosed (trapped) H• atoms is the comparatively large values for the activation energies of their thermal decay. In addition it is noteworthy that the H• atoms fulfill the function of a spin probe in the solid-state samples. Compared to other paramagnetic dopants, such as transition metal ions,^[2–5] the H• atoms are more suitable as a probe because their influence on the matrix is significantly lower. For example, both the spectral and spin dynamic ESR behavior and also the corresponding activation energies calculated from the thermal decay curves (Table 1) allow definitive conclusions to be drawn about the state of order in the matrix. These are in complete agreement with the findings from thermal analysis and X-ray diffraction. This form of direct relationship for trapped H• atoms has not been reported to date.

Table 1. Activation energies E_A and rate constants k for the thermally induced decrease in the H• signal in aluminum fluorides.

Annealing temperature [°C] ^[a]	Annealing time [h]	k ^[b,c] [g mol ⁻¹ min ⁻¹]	E_A [kJ mol ⁻¹]
200	1	0.00576 (80) 0.02797 (110)	59.016
300	1	0.01148 (150) 0.08311 (200)	65.782
400	1	0.01084 (200) 0.06918 (250)	76.290
500	1	0.03668 (250) 0.11399 (280)	91.364
500	10	0.02624 (250) 0.08435 (280)	94.084

[a] The starting materials β -AlF₃·3H₂O were, in each case, annealed in a Q-crucible for 1 or 10 h under quasi isobaric conditions at the temperatures given. Following this they were subjected to γ irradiation. [b] Determined from the time dependent standard signal intensities. [c] The temperature [°C] for the decay reaction is given in each case in parentheses.

[*] Dr. G. Scholz, Prof. Dr. R. Stoer, Dr. J. A. Momand, Dr. A. Zehl, Dr. J. Klein
Humboldt-Universitat zu Berlin
Institut fur Chemie
Hessische Strasse 1–2, 10115 Berlin (Germany)
Fax: (+49)30-2093-7378
E-mail: gs@magneton.chemie.hu-berlin.de

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