

## Preparation of High Purity 1,4-Dioxane, Tetrahydrofuran and Dimethoxyethane as Solvents for Organometallic Compounds

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With 4 Figures

### Summary

1,4-Dioxane, Tetrahydrofuran and Dimethoxyethane were dried over potassium and subsequently degassed, under high vacuum conditions. The u. v. spectra and the electric conductivities of the high purity ethers were measured. The solvents could be stored under high vacuum conditions for an unlimited period of time, without any changes of their physico-chemical properties. Treatment with potassium under high vacuum conditions caused a partial cleavage of the high purity ethers resulting in increased electric conductance and absorption of light.

### Inhaltsübersicht

1,4-Dioxan, Tetrahydrofuran und Dimethoxyäthan wurden unter Hochvakuum-Bedingungen über Kalium getrocknet und anschließend entgast. Die UV-Spektren und die elektrischen Leitfähigkeiten der hochgereinigten Äther wurden gemessen. Die Lösungsmittel konnten unter Hochvakuum-Bedingungen für einen beliebig langen Zeitraum ohne Veränderungen dieser physiko-chemischen Eigenschaften aufbewahrt werden. Behandlung mit Kalium unter Hochvakuum-Bedingungen führte zu einer teilweisen Spaltung der hochgereinigten Äther und hatte eine erhöhte elektrische Leitfähigkeit und Lichtabsorption zur Folge.

Physico-chemical studies of solutions of the potassium compounds of naphthalene, anthracene, di-, tri-, and tetraphenylmethane<sup>2)3)</sup> require the preparation of high purity solvents because of the extreme sensitivity of the organometallic compounds against traces of water and oxygen. These impurities have often led to spectra that are difficult to interpret in all detail.<sup>4)5)</sup>

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<sup>2)</sup> K. K. BRANDES and R. J. GERDES, *J. physik. Chem.* **71**, 508 (1967).

<sup>3)</sup> K. K. BRANDES, R. SUHRMANN and R. J. GERDES, *J. organ. Chem.* **32**, 741 (1967).

<sup>4)</sup> R. SUHRMANN and R. MATEJEC, *Z. physik. Chem. (Frankfurt)* **14**, 246 (1958); *ibid.* **14**, 263 (1958).

<sup>5)</sup> D. F. PAUL, D. LIPKINS and S. I. WEISSMAN, *J. Amer. chem. Soc.* **78**, 116 (1956).

We wish to report that the purification of 1,4-dioxane, tetrahydrofuran, and dimethoxyethane under residual gas pressures in the high vacuum and ultrahigh vacuum range leads to solvents with acceptable physico-chemical properties. These properties can be maintained if the solvents are stored at residual gas pressures of  $10^{-8}$  torr and less.

### Experimental Section

The solvents were prepurified according to the method by PESTEMER<sup>6)</sup>. For further purification the solvents were refluxed repeatedly with sodium wire while a stream of dry nitrogen was passed through. The sodium used for this procedure had been degassed and distilled in a vacuum of  $10^{-3}$  torr. The reflux distillation of the solvents was carried out for 20 hours. After the sodium wire did not show any yellowish color (owing to the polymerization of aldehydes) and also no grayish coating (by oxides and hydroxides) the solvents were rectified. About every two hours the u. v. spectra of the solvents were measured. After the spectra did not change anymore (fig. 1 dashed curves), the solvents were collected in a round bottom flask.

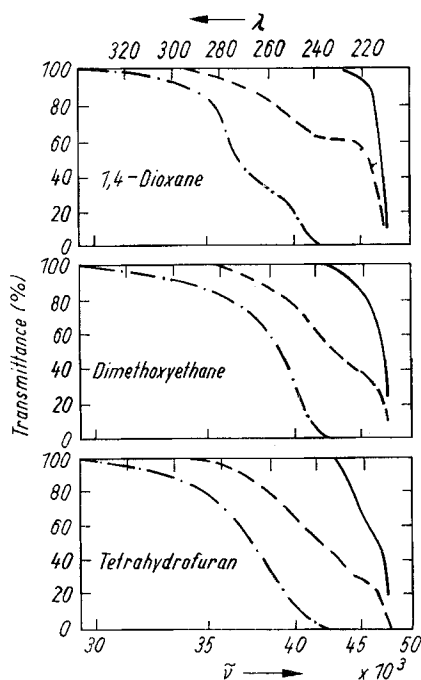


Fig. 1. Transmittance curves for tetrahydrofuran, dimethoxyethane, and 1,4-dioxane. — · — · — commercially available, — — — rectified, — — — purified under high vacuum conditions

In order to remove the main portion of the dissolved gases the round bottom flask was cooled with liquid nitrogen. After all the solvent had become solid, the released gases were pumped off through a cold trap by means of a rotary vacuum pump. After evacuation of the volatile gases, the flask was submerged in a vessel with hot water. The solvent was

<sup>6)</sup> M. PESTEMER, Z. anorg. Chem. **63**, 118 (1951); *ibid.* **67**, 740 (1955).

forced to melt quickly in order to avoid cracking of the flask owing to expansion of the solid solvent. The solidification and evacuation process was repeated several times. Finally the flask was sealed off at S (fig. 2) under a vacuum of  $10^{-3}$  torr. At this point the solvent contained only traces of water, aldehydes, peroxides, and air.

The flask was now attached at  $V_1$  and  $V_2$  to the glass apparatus shown in fig. 2 for further removal of dissolved gases. The glass apparatus was evacuated at a bake-out temperature of  $350^\circ\text{C}$  to a vacuum of  $10^{-7}$  torr. When the glass system had cooled, the solidification and melting process described above was repeated by opening break seal valve  $V_2$  and the ground glass valve, GV. After a residual gas pressure in the  $10^{-7}$  torr range could be maintained,  $S_1$  was sealed off.

The glass apparatus was again evacuated at a bake-out temperature of  $350^\circ\text{C}$  until a vacuum of  $10^{-7}$  torr was obtained. After cooling of the vacuum system, break seal valves  $V_3$ ,  $V_4$ , and  $V_5$  were opened and about 2 g of potassium were distilled out of each of sample tubes  $A_1$ ,  $A_2$ , and  $A_3$  into glass bulbs  $B_1$ ,  $B_2$ , and  $B_3$ . A fairly thick potassium film was formed in each of the glass bulbs. Gases released during this process were pumped off. Now GV was closed, break seal valve  $V_1$  was opened, and the solvent was distilled very slowly through the glass bulbs with the potassium films in the round bottom flask  $RF_2$ . A reaction between potassium and traces of water was only observed in  $B_1$ . The potassium mirrors in  $B_2$  and  $B_3$  remained unchanged. After all of the solvent had distilled into  $RF_2$ , it was solidified with liquid nitrogen. Released hydrogen was pumped off. The flask was then sealed off at  $S_4$  and  $S_5$ .

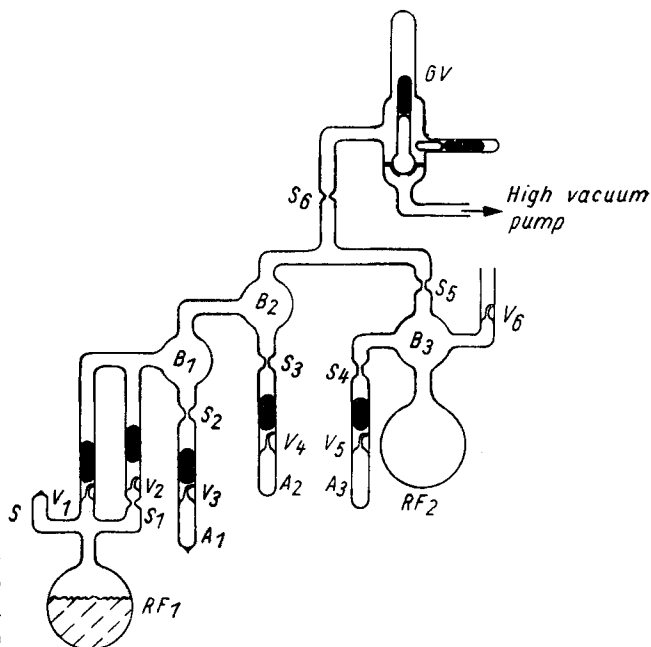


Fig. 2. Degassing and purification in a high vacuum apparatus. After bake out the pressure was well in the ultrahigh vacuum range

High purity potassium was used for the above described purification. The alkali metal was prepared according to the method of DE BOER<sup>7)</sup>.

<sup>7)</sup> J. H. DE BOER, J. BROOS and H. EMMENS, *Z. anorg. allg. Chem.* **191**, 113 (1930).

A mixture of 40 g powdered Zr and  $K_2CrO_4$  was distributed among metal cases made of nickel foil. The nickel cases had been inserted into a glass cylinder which in turn was supported by some glass pieces and sealed into a larger glass tube. After evacuation of the glass apparatus to  $10^{-7}$  torr at a bake-out temperature of  $350^\circ C$ , the mixture was heated to  $900^\circ C$  by means of the work coil of an induction heater. Before the reaction started considerable amounts of gases were desorbed from the zirconium and pumped off. The formed potassium was collected in sample tubes and then sealed off.

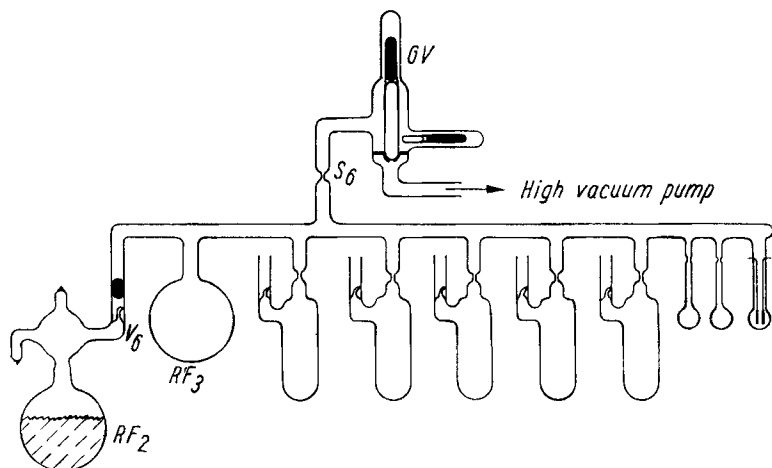


Fig. 3. Final purification and degassing of the solvent and distribution among various sample tubes and cuvettes

The final degassing of the solvents was carried out in a glass apparatus (fig. 3) which had previously been evacuated to  $10^{-7}$  torr at a bake-out temperature of  $350^\circ C$ . Dissolved gases, mainly hydrogen, were released by alternate crystallization and distillation of the solvent through  $V_6$  and between  $RF_2$  and  $RF_3$ . The gases were pumped off through  $GV$ . This procedure was repeated about five to six times until a residual gas pressure of  $10^{-7}$  torr was obtained. Then the glass apparatus was sealed off at  $S_6$  from the high vacuum system and the solvent was distributed for further use among the sample tubes, various cuvettes for spectrometric measurements, and conductivity cells.

## Results and Discussion

The solvents obtained by this method did not absorb any light beyond  $234 m\mu$  (solid curves, fig. 1). The specific conductance of the solvents was: 1,4-dioxane:  $10^{-14} \Omega^{-1} cm^{-1}$ , tetrahydrofuran:  $2 \times 10^{-10} \Omega^{-1} cm^{-1}$ , and dimethoxyethane:  $2 \times 10^{-9} \Omega^{-1} cm^{-1}$ . No changes of these physico-chemical properties were observed when the solvents were stored in sample tubes which were sealed off at a pressure near or in the ultrahigh vacuum range. When 1,4-dioxane was kept for a week over a potassium film in vacuum of  $10^{-7}$  torr no changes of its physico-chemical properties were observed.

However, tetrahydrofuran, stored under the same conditions showed a change of the electric conductance after one week from  $2 \times 10^{-10} \Omega^{-1} \text{ cm}^{-1}$  to  $10^{-7} \Omega^{-1} \text{ cm}^{-1}$ . A considerable change was also noticed in the absorbeny

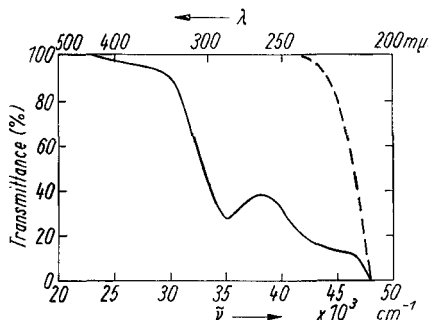


Fig. 4. Transmittance curves for tetrahydrofuran of various degrees of purity. --- ultra-high vacuum purification, — after one week over potassium

of light (fig. 4). Dimethoxyethane showed even greater indications of decomposition. After one day over potassium it became yellowish and cloudy. Apparently, cleavage of the ether by the potassium, with formation of potassium alcoholates and unsaturated hydrocarbons had taken place to a considerable extent.

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