

Fig. 1. The specific volumes of sodium oleate and myristyl sulphate solutions.

- 1 a. Pure sodium oleate solutions.
- 1 b. Sodium oleate solutions saturated with *p*-xylene.
- 1 c. The amounts of *p*-xylene solubilized by sodium oleate solutions.
- 2 a. Pure sodium myristyl sulphate solutions.
- 2 b. Sodium myristyl sulphate solutions saturated with *p*-xylene.
- 2 c. The amounts of *p*-xylene solubilized by sodium myristyl sulphate solutions.

We have also measured the specific volumes of aqueous solutions of these colloids in which *p*-xylene had been solubilized. The specific volumes of series of colloid solutions saturated with *p*-xylene are shown in Fig. 1, curves 1 b and 2 b. The curves are seen to be formed of two almost straight lines which meet at an angle. Calculations based on the measured values show that the break points are due to the fact that the micellar substance is able to solubilize more xylene per mol colloid above than below this concentrations (1 c and 2 c). The break point occurs in the oleate solutions at an oleate concentration of about 7% (0.23 *M*) and in the case of sodium myristyl sulphate at about 7.2% (0.22 *M*). These concentrations are approximately the same as those which according to earlier solubilization studies⁴ represent the 2nd critical concentrations of these associationscolloids.

The data thus confirm that the micelles present below and above the 2nd critical concentration possess different properties as far as their ability to solubilize hydro-

carbons is concerned. Since the partial specific volumes of the colloids in their pure aqueous solutions (without added xylene) are not found to undergo any marked changes in this region, it must be assumed that the packing within the micelles remains unaltered when the mentioned concentration limit is exceeded even though the structures and/or sizes of the micelles may undergo changes.

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Dipole Moment Measurements of α , β , γ , δ and ϵ Benzene Tetrachloride

O. BASTIANSEN and JOAR MARKALI
*Universitetets Kjemiske Institutt,
 Blindern — Oslo, Norway*

By the photochlorination of benzene in the presence of catalytic quantities of iodine, G. Galingaert, A. J. Kolka, H. D. Orloff *et al.* of the Ethyl Corporation, Detroit, have succeeded in isolating five compounds having the structure 3,4,5,6-tetrachlorocyclohexene-1^{1,2}. These five benzene tetrachlorides (BTC) were designated as α , β , γ , δ and ϵ , in the order of their characterization, and the difference between the various isomers was believed to be of the same kind as that known from the benzene hexachlorides (BHC)^{3,4}. Adopting the ideas and designations used for cyclohexane derivatives⁵ the possible configurations of the BTCs can be characterized by the scheme given in Table 1. The "conversion forms" containing more than two ϵ bonds (in parentheses in Table

Table 1. Possible configurations for the BTCs. Calculated dipole moments in Debye.

I	$\kappa \kappa \kappa \kappa \rightleftharpoons (\varepsilon \varepsilon \varepsilon \varepsilon)$	3.06
II	$\varepsilon \kappa \kappa \kappa \rightleftharpoons (\kappa \varepsilon \varepsilon \varepsilon)$	4.88
III	$\kappa \varepsilon \kappa \kappa \rightleftharpoons (\varepsilon \kappa \varepsilon \varepsilon)$	2.89
IV	$\varepsilon \varepsilon \kappa \kappa \rightleftharpoons \kappa \kappa \varepsilon \varepsilon$	3.10
V	$\varepsilon \kappa \kappa \varepsilon \rightleftharpoons \kappa \varepsilon \varepsilon \kappa$	4.03 \rightleftharpoons 0.39
VI	$\varepsilon \kappa \varepsilon \kappa \rightleftharpoons \kappa \varepsilon \kappa \varepsilon$	5.74

1) are rather improbable according to experiences from cyclohexane chemistry⁶. Because of the $1\varepsilon-3\varepsilon$ -repulsion also known from cyclohexane chemistry the isomer (VI) is less probable than the other five. We shall, therefore in the following exclude the forms inclosed within parentheses in Table 1 and suppose that the five known isomers are to be found among the first five possibilities listed in the table.

In the last column of Table 1 we have listed the dipole moments calculated for the free undistorted molecules. The dipole moments of the forms in parentheses are not given. In the undistorted molecules we have assumed that the >C-CHCl-CHCl-C< group of the molecules is arranged as a corresponding group in the BHCs and that the >-CCH=CH-C< group is planar. The partial moments of the C-Cl bonds are for the sake of simplicity assumed to be the same in all positions and forms. We have chosen for the partial moment the value 2.10 D as found for monochlorocyclohexane in benzene solution⁷.

In Table 2 we have listed the dipole moments of the BTCs measured in benzene solution. In accordance with common experience we find that the calculated values on an average are greater than the measured. However, if we assume that the sequence of the measured and the calculated values is the same we can conclude that the known isomers have the following forms α ($\varepsilon \varepsilon \kappa \kappa$), β ($\varepsilon \kappa \kappa \varepsilon$), γ ($\varepsilon \kappa \kappa \kappa$), δ ($\kappa \kappa \kappa \kappa$) and ε ($\varepsilon \kappa \varepsilon \kappa$).

The dipole moment measurements indicate that the β isomer has the form V

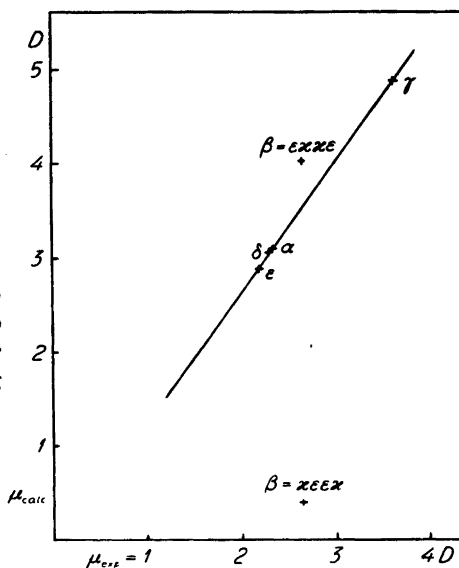


Fig. 1. Calculated dipole moments of α , β , γ , δ and ε BTC plotted against the experimental dipole moments.

Table 2. Measured dipole moments for α , β , γ , δ and ε BTC.

Isomers	Measured dipole moments in Debye
α	2.34
β	2.65
γ	3.62
δ	2.30
ε	2.19

(Table 1) and that the configuration $\varepsilon \kappa \kappa \varepsilon$ is the predominating one. We can not, however, exclude the possibility of some contribution from the $\kappa \varepsilon \varepsilon \kappa$ form. As a matter of fact the dipole moment measurements do indeed indicate the presence of an equilibrium with some contribution from the latter form. In Fig. 1 we have plotted the measured dipole moment as the abscissa and the corresponding calculated value as the ordinate. We see that all points except that of the β isomer lie practically on a straight line indicating

that the measured and calculated values are approximately proportional for the α , γ , δ and ϵ isomer. To bring the point of the β isomer onto the straight line we have to assume an equilibrium $\epsilon \kappa \kappa \epsilon \rightleftharpoons \kappa \epsilon \epsilon \kappa$ with approximately 87 % contribution from the former and about 13 % contribution from the latter form.

Because of the small differences between the dipole moments of the α , δ and ϵ isomers and because of the rather uncertain assumption of the undistorted molecules the dipole moments measurements must not be regarded as conclusive for the structure of these three isomers. The results are, however, in accordance both with the results of the Ethyl Corporation team² and with the electron diffraction work done at our institute. The electron diffraction work which is going to be published soon in this journal establishes the structure of the α , δ and ϵ isomers and excludes the presence of the $\epsilon \kappa \epsilon \kappa$ form and any appreciable contribution from the forms containing more than two ϵ bonds. The electron diffraction work thus demonstrates the validity of the assumptions on which the present discussion is based.

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On the Tantalum — Oxygen System

STIG LAGERGREN and ARNE MAGNËLI

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

Through the chemical and X-ray investigations on the niobium-oxygen system, carried out by Brauer¹ a decade ago, the occurrence of the phases NbO, NbO₂, and Nb₂O₅ (three modifications) was established while the oxides Nb₂O, Nb₂O₃, and Nb₃O₅ reported by previous authors were shown not to exist. There are also a number of tantalum oxides described in literature, viz. TaO, Ta₂O₃, TaO₂, and Ta₂O₅. Among these compounds, however, the pentoxide is the only one, whose existence has been firmly established. As a systematic investigation of the tantalum-oxygen system was lacking, we decided to study this matter.

The starting materials for the investigation were tantalum powder and tantalum pentoxide (both of Fansteel manufacture), weighed amounts of which were intimately mixed, pressed to pastilles and heated in vacuo. The products were investigated by taking X-ray powder photographs using a Guinier focusing camera with monochromatized Cu-K α radiation.

It has recently been found that niobium and niobium pentoxide readily react to form intermediate oxides when heated for one or two days at 1 000–1 100° C in sealed off silica tubes*. When mixtures of tantalum and tantalum pentoxide were correspondingly treated, no reaction could be observed even after rather intense heating (1 100° C for ten days or 1 250° C for two days).

In order to obtain higher temperatures a vacuum high frequency induction fur-

* Private communication from Dr. Beryl M. Oughton.