

stirred at 40° in a 3-litre three-necked flask for 20 h.

The resulting mixture is distilled under reduced pressure (about 60 mm Hg) to remove the excess of 2,3-dibromopropene. About 240 ml are thus recovered. The residue in the flask is filtered and washed with a small quantity of petroleum ether.

The product is dissolved in an ice-cold solution of 65 g of sodium hydroxide in 2 500 ml of water. An insoluble residue of about 10 g is filtered off. The solution is treated with discolouration carbon and then 10 g of ethylenediaminetetraacetic acid are added to remove cupric ions. The filtered solution is carefully added to 150 ml of concentrated hydrochloric acid. The product is filtered off, washed with water and recrystallized from methanol. The yield is 235 g (68 %) of a pure white product with a melting point of 144.8°–145.0°.

In exactly the same way the compounds in Table 2 are prepared.

The author is indebted to his colleagues and assistants at Pharmacia for good help with this project.

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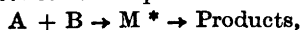
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On the Relation between the Reaction Velocity and Dielectric Constant of the Medium

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According to Laidler and Eyring¹, the effect of the dielectric constant of the solvent on the rate of a bimolecular reaction between two dipole molecules A and B,



can be expressed by the equation

$$\ln k = \ln k_0 - \frac{1}{kT} \frac{D-1}{2D+1} \left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_s^2}{r_s^3} \right) + \frac{\Sigma \Phi}{kT} \quad (1)$$

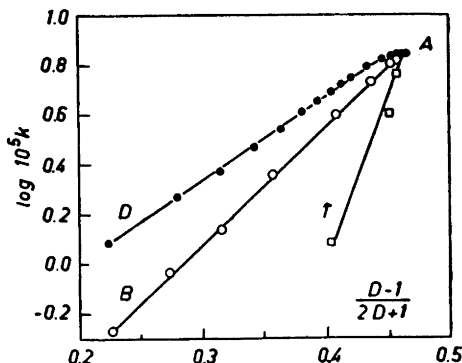


Fig. 1. Plot of $\log k$ for the reaction $(C_2H_5)_3N + C_2H_5I \rightarrow (C_2H_5)_4NI$ against $(D-1)/(2D+1)$ at 25°. A = acetone, B = benzene, D = dioxan, T = tetrahydrofuran.

where k and k_0 are the rate constants in a medium of dielectric constant D and in a medium of dielectric constant unity, respectively. The μ 's and r 's are the dipole moments and radii of the reactants and transition state, respectively. If the non-electrostatic term $\Sigma \Phi/kT$ is small enough to be neglected, and if μ_s^2/r_s^3 is independent of the medium, the plot of $\log k$ against $(D-1)/(2D+1)$ should be a straight line for the same reaction carried out in different media. Linear plots were obtained for the reactions between pyridine and benzyl bromide and between triethylamine and benzyl bromide in benzene-ethanol mixtures, but not in benzene-nitrobenzene mixtures¹. In cases where solvation phenomena play an important role, examination over larger areas of solvent mixtures has in general shown departure from linearity.

In Fig. 1 the eqn. (1) has been tested upon the results of some recent investigations concerning quaternary ammonium salt formation, viz. the reaction between triethylamine and ethyl iodide in acetone-benzene, acetone-dioxan, and acetone-tetrahydrofuran mixtures. The rate constants for 25° were calculated by the Arrhenius equation from the data of Tommila and Kauranen². The dielectric constants of acetone-benzene mixtures were taken

from the measurements of Drude³ and those for acetone-dioxan and acetone-tetrahydrofuran mixtures from a recent communication of Lindberg⁴. It is seen that in acetone-benzene mixtures the plots are linear within the limits of experimental error over the whole range of the mixtures. In acetone-dioxan mixtures there is at 25° a weak deviation from the rectilinear course in the range from pure acetone to 12 % dioxan, but from the values of the rate constant one can conclude that this deviation disappears at 40° and higher temperatures. In acetone-tetrahydrofuran mixtures the number of kinetic data is too small for definite conclusions, but it seems probable that in this solvent system the plot is also linear over the whole range of mixtures.

The slope of the plots shows that in eqn. (1) the last term in the brackets is greater than the sum of the first two terms. This is quite natural, since the final products of the reaction are ionized and, accordingly, it is reasonable to assume that the dipole moment of the transition complex is large. The different slopes of the plots show that the term in brackets has different values for the three solvent systems.

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The Structure and Synthesis of Cycloalliin Isolated from

Allium cepa

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Some years ago we¹ isolated from a 70 % ethanol extract of onion after hydrolysis with 6 N HCl the crystalline hydrochloride

of a sulphur-containing amino acid $C_6H_{11}O_2NS \cdot HCl$. Before hydrolysis it was not found in onion. This amino acid could be oxidized by 30 % hydrogen peroxide in glacial acetic acid to the corresponding sulfoxide which was isolated as the crystalline hydrochloride $C_6H_{11}O_2NS \cdot HCl \cdot H_2O$ (Virtanen and Bramesfeld). Because the sulfoxide could be reduced with Raney nickel back to $C_6H_{11}O_2NS$ it was clear that an amino acid sulfoxide and its thioether were in question.

Later on the sulfoxide was found as an original amino acid in onion². The first isolated S-amino acid was obviously formed from the sulfoxide on treatment with strong hydrochloric acid. The amino acid sulfoxide was isolated from a 70 % ethanol extract of onion. The elementary composition of the isolated and recrystallized amino acid hydrochloride corresponded to the formula $C_6H_{11}O_2NS \cdot HCl \cdot H_2O$. (Found: C 31.31; H 6.37; N 5.90; S 13.60; Cl 15.20. Calc. C 31.09; H 6.09; N 6.04; S 13.84; Cl 15.31.) On spraying with ninhydrin it gives a greenish blue spot, its reduced S-compound a violet one, on the paper chromatogram. The sensitiveness of of the colour reaction of the sulfoxide is about 1/20, and that of the S-compound about 1/10, of that of alanine. R_F -values for the sulfoxide: 0.85 in phenol- NH_3 , 0.15 in butanol-acetic acid-water, and for the S-compound: 0.90 in phenol- NH_3 , 0.48 in butanol acetic acid-water². Sulfoxide $[\alpha]_D^{20} -17.4^\circ$ (in water).

There is no double bond and also no primary amino group in either of the amino acids. The nitrogen belongs to an imino group. On the basis of these facts and the elementary composition of the substance it should contain a heterocyclic ring.

Detailed investigations of the products formed by heating of the sulfoxide with 6 N HCl at 105°C for 43 h elucidated the structure of this compound. As reduction products the corresponding thioether (II) and as oxidation products 2-aminopropane-1-sulphonic acid (2-methyltaurine) (III) and cysteic acid (IV) were formed. In addition a small spot in the solvent front (phenol), probably an amine, was found on the paper chromatogram (Fig. 1). These results led to structure I for the sulfoxide and structure II for the thioether^{3,4}.

The elementary composition of compound III corresponded to the formula $C_6H_{11}O_2NS$. Paper chromatographically it was identical with synthetic 2-methyltauri-