largely due to conformational energy differences between the transition states in question. The preferred conformation of the intermediate I^+ should be similar to that of propionaldehyde, in which the methyl group is eclipsed with the double bond,[6] or, in our case, with the partial double bond of the intermediate. In the case of a *cis* compound, this conformation is already present in the transition state, whereas in the transition state derived from the *trans* form, it is a hydrogen atom that is eclipsed with the partial double bond, and the more favorable conformation is not achievable in the transition state because the central carbon-carbon linkage has not completely lost its double bond character.

Table 3 shows values of the deuterium solvent isotope effect for some of the vinyl ethers studied and the value of Kresge and Chiang[7] for ethyl vinyl ether. It is interesting to note that the isotope effect decreases with increasing methyl substitution. This results probably from the above-mentioned factors that bring about the changes in the hydrolysis rates with methyl substitutions, although more extensive information is needed to elucidate this point in detail.

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Received May 18, 1967.

The Purification of N,N-Dimethylformamide and Acetonitrile for Polarographic Use

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The sensitivity of the polarographic method makes the purity of the solvent a question of importance. As regards N,N-dimethylformamide and acetonitrile, the most widespread solvents in non-aqueous polarography, several methods of purification are reported in the chemical literature.[1-4] However, as a rule these methods are not entirely satisfactory. Either the product is not very pure or the method is laborious. The methods of purification developed by the author yield, with very little work, products with a high degree of purity. As a consequence, very pure solvents can be used even in preparative electrochemistry thus facilitating the identification of the products.

N,N-Dimethylformamide (DMF). This solvent is purified by treatment with active alumina: A separatory funnel with a wide bore stopcock is connected with a ground glass joint to a chromatography column, the stem of the funnel intruding approximately 15 cm into the column. The column is equipped with a fine porosity sintered glass filter and a Teflon key stopcock, leading through a ground glass joint into the receiving flask. Rubber tubing connects the receiving flask and the upper part of the column to a drying tower.

The apparatus is thoroughly dried and filled with dry nitrogen. The column is then filled with alumina. Woelm aluminium oxide, activity grade one, is the only one found effective. The separatory funnel is mounted and filled with DMF, previously dried over molecular sieves (Linde, 4A). After removal of the nitrogen with a vacuum pump, the column is filled with DMF from the funnel. During this operation dry nitrogen is led to the top of the funnel. The funnel is stoppered, and a constant niveau of DMF in the column is maintained by leaving the funnel stopcock open. If the first filling of the column is made with high purity DMF, the bottom stopcock of the column can be left open. If ordinary DMF is used, the bottom stopcock should be closed for a day or two before the column is

allowed to operate. A column approximately 100 cm long and 5 cm wide will contain 1 kg of alumina, sufficient for the purification of about 10 l of DMF. With this column a drop rate of approximately one drop per five seconds has been found to give a pure product.

After passing the column, the DMF smells strongly of amine. The amine is eliminated by bubbling pure nitrogen through the DMF for several hours. The resultant product shows two peaks in gas-liquid chromatography, the smaller of which is 100 ppm of the bigger one (90°C, stationary phase: polypropylene glycol). Polarography shows no defined wave, but a residual current of approximately 0.02 μA. The water content has been measured by Karl Fischer titration. Up to about 100 ppm of water has been found.

Acetonitrile. Acetonitrile is obtained as a byproduct in the manufacture of acrylonitrile, which is the main impurity in commercial acetonitrile. The difference in boiling points of these two compounds is only 4.2°C, so the complete separation by normal fractional distillation is practically impossible. The author has found, however, that separation is possible by distillation of the ternary and secondary azeotropes the two liquids form with ethanol and water.

In a typical run 300 ml of 96 % ethanol was added to 3.5 l of commercial acetonitrile and the mixture was distilled on a Stedman column using an automatic take-off head. The column is 110 cm long, with inner diameter 2.5 cm and equals 60–65 theoretical plates. With a reflux ratio of 80, the distillate was pure after nine days of distillation. Total yield of pure acetonitrile: approximately 1.5 l. The purity was measured by gas-liquid chromatography and by polarography. Gas chromatography shows two peaks, the smaller of which is 60 ppm of the bigger one. (65°C, stationary phase: polypropylene glycol). Polarography shows a residual current of about 0.01 μA.

Provided the joints by which the receiver is connected to the column are not greased the pure acetonitrile is also well suited for ultraviolet spectroscopy.[2]

Acknowledgement. The author wants to express his gratitude to Professor K. A. Jensen for his kind interst in this work.

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Received March 9, 1967.

Spectroscopic Studies on Metal Carbonyls

VI. Mean Amplitudes of Vibration and Shrinkage Effects for Iron Pentacarbonyl

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This paper continues the series on metal carbonyls wherein the previous papers[1-3] have given spectroscopic calculations for the chromiun and molybdenum hexacarbonyls, and for nickel tetracarbonyl.

The trigonal bipyramidal symmetry of the iron pentacarbonyl molecule is in accordance with electron diffraction studies,[4,5] X-ray crystallographic calculations,[6] and the numbers of infrared and Raman fundamentals.[7] Fateley and Lippincott,[8] and Kawai and Murata [9] have carried out normal coordinate analyses, and given symmetry force constants [8] and Urey-Bradley force constants.[9] In this paper fundamental frequencies given by Edgell *et al.*[7] were adopted. Two fundamentals, the A_2' frequency (ν_5) and one of the A_2'' frequencies (ν_9), not given by Edgell *et al.* were taken from Fateley and Lippincott's paper.[8] Symmetry force constants were computed, with the assumption of zero values for all the off-diagonal elements. By means of this force field the mean amplitudes of vibration (Table 1) and Bastiansen-Morino shrinkage effects (Table 2) were computed. In the tables "(eq)" and "(ax)" refer to "equatorial" and "axial" distances, respectively. The equilibrium distances used are given in parentheses. Both types of C=O bond distances, equatorial and axial, were given the same equilibrium