Dipole Moments of the Chlorobenzophenone Oximes

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Uncertainty concerning the mechanism of the Beckmann rearrangement makes it highly desirable to find some method, independent of the rearrangement, for determining the configurations of the isomeric oximes. A few attempts have been made to accomplish this by dipole moment measurements. Hassel and Naeshagen made the first study of this kind.[1] They used benzaldoxime and acetaldoxime in benzene solution but abandoned the plan on account of the tendencies of the oxime molecules to associate. Sutton and Taylor sought to overcome this difficulty by using the N-methyl ethers of oximes.[2] There is, however, the remote possibility that *cis–trans* isomerization occurs in the process of forming the N-ether. There is no strict guarantee that an ether corresponds in structure to the oxime from which it is derived.

We have measured the dipole moments of the *ortho* and *para* chlorobenzophenone oximes in dioxane—a solvent in which the free oximes have little tendency to associate. The two oximes derived from *m*-chlorobenzophenone were measured in benzene and in carbon tetrachloride before we found that dioxane was a better solvent. Since we do not intend to continue this work we include in this paper the average values of the dipole moments of the *meta* compounds as measured in benzene and carbon tetrachloride although there was evidence of association in both of these solvents and the numbers reported cannot be true values. For the purpose of this investigation the absolute values of the moments are not required. The point of interest is to find out which member of the pair of oximes has the higher moment.

The apparatus comprised a crystal controlled oscillator operating at a frequency of 500 kilocycles, another oscillator the frequency of which was determined by a fixed inductance and a precision variable condenser, a radio receiving set and a source of constant frequency sound waves. The method has been described in detail by Williams and Weissberger,[3] Smyth,[4] Zahn[5] and others.

Dioxane freezes at 11° and the oximes decompose rapidly above 50°. The available temperature range, therefore, was too narrow to permit a calculation of the dipole moment by elimination of the P_A and P_E factors by dielectric constant measurements at different temperatures. We used, therefore, the refractive indices of the solutions to supplement the polari-

(1) Hassel and Naeshagen, Z. physik. Chem., **4B**, 217 (1929).

(2) Sutton and Taylor, J. Chem. Soc., 2190 (1931).

(3) Williams and Weissberger, THIS JOURNAL, **50**, 2332 (1928).

(4) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York.

(5) Zahn, Phys. Rev., **24**, 400 (1924).

zation measurements and we assumed that in the equation $P = P_E + P_A + P_M$ the term P_A (atomic polarization) would be the same for each member of a pair of isomeric oximes. The refractive indices were measured with a Pulfrich refractometer which was kept at constant temperature by circulating water from a thermostat. The pycnometers used in the density measurements were brought to the same temperature by immersion in the same thermostat bath.

Our values for the dipole moments are as follows

o-Chlorobenzophenone oximes: α-form (m. p. 131°) 161×10^{-18}, β-form (m. p. 96–97°) 161×10^{-18} e. s. u.

p-Chlorobenzophenone oximes: α-form (m. p. 162–164°) 2.320×10^{-18}, β-form (m. p. 91–92°) 2.381×10^{-18} e. s. u.

m-Chlorobenzophenone oximes: α-form (m. p. 132–133°) 1.50×10^{-18}, β-form (m. p. 105–106°) 1.61×10^{-18} e. s. u.

In all cases where members of the isomeric pairs show different polarizations, the higher melting form has the lower dipole moment and in every case the high-melting form rearranges to yield an amide in which the unsubstituted phenyl group is found attached to the nitrogen atom.

These results do not give an unambiguous answer to the question of oxime structures. The measured moment is the vector sum of several moments in the molecule. The difference between the values for the two members of a pair of oximes may be attributed definitely to the *cis* and *trans* configurations but we do not know the direction of the resultant of the vectors between the nitrogen and oxygen atoms and between the hydrogen and oxygen atoms. If the hydroxyl group as a whole is positive with respect to the nitrogen atom, these measurements support the Meisenheimer mechanism of the Beckmann rearrangement.[6] If the negative end of the resultant dipole is toward the hydroxyl group, these results support the original view of Hantzsch.[7]

Summary

The dipole moments of the six oximes obtainable from monochlorobenzophenone have been measured with sufficient accuracy to determine the relative values in the three pairs of *cis–trans* isomers. Within the limits of accuracy obtainable with our equipment the two *ortho* compounds have identical moments. The higher melting forms of the *meta* and *para* compounds have the lower dipole moment.

The chlorinated phenyl group shifts to the nitrogen atom when the low-melting form is subjected to the Beckmann rearrangement. The unsubstituted phenyl group migrates when the high-melting oxime undergoes the Beckmann change.

(6) Meisenheimer, *Ber.*, **54**, 3206 (1921).

(7) Hantzsch, *ibid.*, **24**, 22 (1891).