The Determination of the Barrier to Internal Rotation in Ferrocene and Ruthenocene by Means of Electron Diffraction

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BOHN and HAALAND[1] have shown by means of electron diffraction that the free ferrocene molecule has an eclipsed (D_{5h}) equilibrium conformation with a small barrier to internal rotation. They estimated the barrier to be about $V_0 = 1{\cdot}1$ kcal./mole, but no error limits were given. We have now extended the range of observed intensities beyond that obtained by Bohn and Haaland, and by means of a new computer programme we have been able to refine the barrier height by least-squares calculations.

The scattering pattern from gaseous ferrocene at about 140° was recorded on the Oslo electron diffraction units.[2] The resulting experimental modified molecular intensity curve extended from $s = 0{\cdot}5$ Å^{-1} to $s = 53{\cdot}75$ Å^{-1}. [$s = (4\pi\sin\theta)/\lambda$, where θ is half the diffraction angle and λ the electron wavelength].

The contribution of each atom pair, i, j, in the molecule to the theoretical modified molecular intensity curve was first calculated according to equation (1) where $f_j(s) = |f_j(s)| \exp[(i\eta_j(s)]$ is the complex atomic scattering factor of atom j. R_{ij} is the internuclear distance and u_{ij} the r.m.s. amplitude of vibration.

The molecular structure was first refined by least-squares calculations on the intensity data[3] under the assumption that the molecule is staggered. The resulting square-error sum was 2·60. The structure was then refined under the assumption that the molecule is eclipsed. The resulting square-error sum was 1·77. The values obtained for the bond distances and for the vibrational amplitudes of distances not affected by internal rotation were nearly identical in the two refinements.

The Schrödinger equation for internal rotation[4] in ferrocene was solved for

$$V(\phi) = \tfrac{1}{2}V_0[1 - \cos(5\phi)]$$

with values of V_0 ranging from $-7{\cdot}0$ to $+7{\cdot}0$ kcal./mole. The isomuthal angle $\phi = 0$ for one

$$I_{i,j} = \frac{|f_i(s)|\ |f_j(s)|}{|f_{\mathrm{C}}(s)|^2} \cos[\eta_i(s) - \eta_j(s)]\, \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2) = g_{ij/\mathrm{CC}}(s)\, \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2) \qquad (1)$$

TABLE

β	A	C(Å)†	D(Å)†	V_0(kcal./mole)
$-0{\cdot}20$	0·61	0·110	$-0{\cdot}004$	$0{\cdot}99 \pm 0{\cdot}38$
$-0{\cdot}10$	0·58	0·110	$-0{\cdot}004$	$0{\cdot}95 \pm 0{\cdot}35$
0·00	0·56	0·110	$-0{\cdot}004$	$0{\cdot}91 \pm 0{\cdot}32$
$+0{\cdot}10$	0·54	0·110	$-0{\cdot}004$	$0{\cdot}87 \pm 0{\cdot}30$
$+0{\cdot}20$	0·52	0·110	$-0{\cdot}004$	$0{\cdot}84 \pm 0{\cdot}28$

† Standard deviation = 0·007—0·008 Å.

of the eclipsed conformations. Hence $V_0 < 0$ corresponds to a staggered and $V_0 > 0$ to an eclipsed minimum energy conformation. An angular probability function $W(\phi)$ was defined such that the probability of the isomuthal angle being between ϕ and $\phi + \mathrm{d}\phi$ is equal to $W(\phi)\mathrm{d}\phi$:

$$W(\phi) = N\sum_i \exp(-\epsilon_i/kT)\psi_i^2(\phi)$$

N is a normalizing constant. It was found that, for $T = 413°$ K and V_0 in the range indicated, the angular probability function obtained in this manner was indistinguishable from

$$W'(\phi) = N'\exp[-V(\phi)/kT]$$

We have assumed that classical statistics can be used for other shapes of the barrier too, so that a barrier of the form

$$V(\phi) = \tfrac{1}{2}V_0[1 - \cos(5\phi) - \beta\cos(10\phi)]$$

will give the angular probability function

$$W''(\phi) = N''\exp[A(\cos5\phi) + \beta\cos(10\phi)] \qquad (2)$$

with $A = V_0/2kT$.

The contribution from pairs of carbon atoms in different ligand rings to the modified molecular intensity was next calculated according to

$$I_{\mathrm{C}\ldots\mathrm{C}'}(s) = \int_0^{2\pi} W''(\phi)\,\frac{\sin[r(\phi)s]}{r[\phi]}\,\exp\left[-\frac{1}{2}u_{\mathrm{f}}^2(\phi)s^2\right]\mathrm{d}\phi \qquad (3)$$

where $r(\phi)$ is the internuclear distance as a function of the isomuthal angle, and $u_{\mathrm{f}}^2(\phi)$ is the mean-square amplitude resulting from all modes of vibration except libration.[5] Morino and Hirota[5] have plotted $u_f(\phi)$ for the Cl . . . Cl′ distance in $\mathrm{Si_2Cl_6}$. The curve suggests a variation of the form:

$$u_{\mathrm{f}}(\phi) = C + D\cos\phi \qquad (4)$$

The contribution from all other atom pairs to the molecular intensity was calculated from equation (1) with the values of R and u obtained by refinement on the eclipsed model.

A computer program was written which allowed the parameters A, C, and D to be refined simultaneously by least-squares calculations on the intensity data along with the scale factor. The results of refinements with different values of β are given in the Table.

It is seen that the value obtained for the barrier height is remarkably insensitive to the shape assumed (β). This conclusion was amply confirmed when refinements were carried out with expressions for W and u_f quite different from those in equations (3) and (4).

We therefore conclude that the equilibrium conformation of the free ferrocene molecule is eclipsed and that the barrier to internal rotation $V_0 = 0{\cdot}9$ kcal./mole with a standard deviation $= 0{\cdot}3$ kcal./mole.

The investigation of ruthenocene was less successful. Due to the heavy background of atomic scattering from Ru, the molecular intensity could not be measured as accurately as for ferrocene, and the contribution from inter-ring C · · · C′ distances to the molecular intensity is also relatively smaller than in ferrocene.

The scattering pattern from the gas at about 140° was recorded over the range $s = 0{\cdot}50$ to $46{\cdot}00$ Å^{-1}. Refinement on the staggered model gave a square-error sum of 1·86, refinement on an eclipsed model a square-error sum of 1·65. Refinement of the barrier gave $V_0 = 26 \pm 49$ kcal./mole. Hence it is only possible to conclude that an eclipsed equilibrium conformation is the most probable.

(*Received, November 8th*, 1967; *Com.* 1210.)

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