Equilibrium structure of maleic anhydride from gas-phase electron diffraction (GED) and quantum-chemical studies

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ABSTRACT

The molecular structure of maleic anhydride was reinvestigated by the gas-phase electron diffraction (GED) method because it was determined with large uncertainties in a previous study. To take into account vibrational effects, the corrections to the experimental bond lengths (r_a) were calculated using quadratic and cubic force constants from high-level ab initio calculations (MP2/aug-cc-pVTZ). The determined equilibrium structural parameters (r_e(C–C) = 1.485(1) Å, r_e(C=C) = 1.332(1) Å, r_e(C–O) = 1.386(1) Å, r_e(C=O) = 1.192(1) Å, $\angle_e$(C–C=C) = 107.8(1)°, $\angle_e$(O=C–C) = 129.2(2)°) are very close to the parameters of the r_s structure from a previous microwave spectroscopic (MW) study. Some aspects of the combined analysis of GED and MW data are discussed. The agreement of the experimental rotational constants, $B_0^{(i)}$ (MW), corrected for anharmonic effects, $B_e^{(i)}$ (MW), with the rotational constants derived from the determined equilibrium geometry, is better than with $B_e^{(i)}$ values from quantum-chemical calculations.

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1. Introduction

Going to determine the molecular structure of maleic acid by the gas-phase electron diffraction (GED) method we find out that this substance essentially decomposes at the experimental temperature into maleic anhydride. The mass-spectrometric analysis based on the chemical ionization method confirmed this result. To assume the structure of the anhydride in the mixture of the decomposition products of the acid, it should be determined first in an independent experiment. The maleic anhydride structure was already studied by the GED method at a nozzle temperature of 90 °C [1]. However, several structural parameters were obtained with large uncertainties (up to 0.03 Å and 3° for bond lengths and bond angles, respectively). Moreover, the determined thermal-average structure is not free from vibrational effects. Therefore, it should be different from that at other temperatures and cannot be correctly compared with structures of other types, for example, with the isotopically substituted structure (r_s) from microwave spectroscopic (MW) study [2], the equilibrium geometry (r_e) from

quantum-chemical calculations, etc., as having different physical meaning. The purpose of the present study is the reinvestigation of the molecular structure of maleic anhydride by the GED method and the determination of the equilibrium structure taking into account vibrational corrections calculated from MP2/aug-cc-pVTZ quadratic and cubic force field. Moreover, problems of the combined analysis of GED and MW data will be discussed. The rotational constants derived from the determined equilibrium geometry will be compared with the MW spectroscopic data [2,3].

2. GED experiment

The maleic anhydride sample was purchased from Sigma–Aldrich Co. (purity >99%) and used without further purification. The GED experiment was carried out in the Moscow State University on the EG-100 M apparatus. The experimental conditions were the following: accelerating voltage of *ca.* 60 kV, electron beam current of 1.6...1.9 μA, vacuum of 5×10^{-6} mm Hg. The sample was evaporated from a stainless steel cell by heating to 67(5) °C. The diffraction patterns were recorded on photo films (MACO EM-FILM EMS) at the long (LD) and short (SD) nozzle-to-film distances of
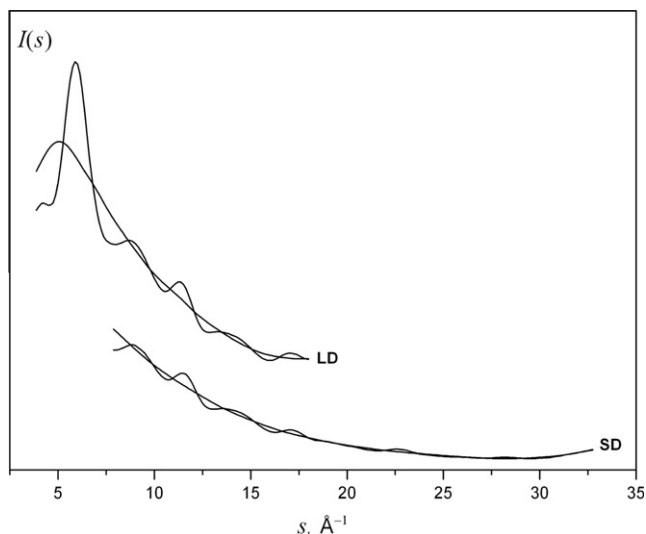
Fig. 1. Experimental intensity curves $I(s)$ with background lines for the long (LD) and short (SD) nozzle-to-film distances.

362.28 and 193.94 mm, respectively. The wavelength of the electrons λ was calibrated using CCl_4 as standard with structural parameters taken from Ref. [4]. The fluctuation of the wavelength of electrons during each experiment (LD and SD) was less than 0.02%. The diffraction patterns were scanned on the calibrated Epson Perfection 4870 commercial scanner (in the 300 dpi scanning mode). The scanned data were transformed into intensity curves $I(s)$ using the procedure described elsewhere [5].

The averaged experimental intensities $I(s)$ were obtained in the ranges of $s = 3.875 - 18.000\ \text{Å}^{-1}$ (LD) and $s = 7.750 - 32.750\ \text{Å}^{-1}$ (SD) with steps of $0.125\ \text{Å}^{-1}$. They are presented together with background lines in Table 1S of Supplementary material and in Fig. 1.

3. Quantum-chemical calculations

Quantum-chemical calculations were carried out by means of the GAUSSIAN03 (Rev.E.01) program package [6] running under a

Linux operating system on a cluster of quad-core Intel Xeon processors (University of Ulm, Group of Chemical Information Systems). The molecular structure of maleic anhydride was optimized at the B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory (see Table 1). The optimized geometries and corresponding rotational constants are presented in Tables 1 and 2, respectively. The equilibrium conformation of C_{2v} symmetry was confirmed by frequency calculations. The calculated frequencies are presented in Table 2S of Supplementary material in comparison with the experimental data from literature [7]. The harmonic and anharmonic (cubic) force constants were calculated at the MP2/aug-cc-pVTZ level.

4. Structural analysis of the GED data with use of experimental rotational constants and MP2/aug-cc-pVTZ force field

The GED molecular model of C_{2v} symmetry (Fig. 2) was described by the following eight structural parameters: five bond lengths, C–C, C=C, C–O, C=O and C–H, and three bond angles, C–C=C, O=C–C and C=C–H (see Table 1). The analysis of the GED data was performed in terms of the equilibrium r_e structure which was derived from the conventional thermal–average parameters $r_{ij,a}$. These transformations as well as the calculations of the root-mean-square (rms) vibrational amplitudes were carried out taking into account nonlinear kinematic effects at the level of the first-order perturbation theory [8,9]. The harmonic ($\delta_{ij,h1}$, including also centrifugal distortions due to vibrations [10]) and anharmonic ($\delta_{ij,anh1}$ [9]) corrections were calculated using quadratic and cubic force constants, respectively, from MP2/aug-cc-pVTZ calculations by means of SHRINK-07 program written by V.A. Sipachev (for more details see also [11]). Corrections for the centrifugal distortion effects due to the overall rotation ($\delta_{ij}^{cent,rot}$ [12]) were also included. The total corrections $\Delta(r_{ij,e} - r_{ij,a})$ and the rms amplitudes $u_{ij,h1}$ are listed in Tables 3 and S3 (Supplementary material), respectively.

The experimental amplitudes u_{ij} were refined in groups as shown in Table S3 of Supplementary material. Differences between amplitudes in each group were assumed at the values derived from the theoretical amplitudes, $u_{ij,h1}$. The amplitudes for hydrogen containing bond lengths were not refined and were kept at the calculated values. Since the $u(O6...O7)$ amplitude could be determined

Table 1
Structural parameters of maleic anhydride as determined by different methods[a].

Parameter	r_e (GED) I	r_g (GED) II	r_e (GED) III	r_e (GED + MW) IV	r_g (GED + MW) V	r_g (GED)[b] VI	r_s (MW)[c] VII	r_e B3LYP[d] VIII	r_e MP2[d] IX
C–C	1.485(6)	1.495(6)	1.487(2)	1.485(1)	1.495(1)	1.500(5)	1.4849(3)	1.4871	1.4846
C=C	1.339(6)	1.348(6)	1.332(1)[e]	1.332(1)[e]	1.341(1)	1.330(30)[f]	1.3331(4)	1.3285	1.3364
C–O	1.380(2)	1.389(2)	1.386(1)[e]	1.386(1)[e]	1.396(1)	1.394(11)	1.3876(1)	1.3912	1.3912
C=O	1.190(2)	1.195(2)	1.193(1)	1.192(1)	1.197(1)	1.195(3)	1.1962(1)	1.1901	1.1978
C–H	1.162(19)	1.182(19)	1.078[g]	1.078[g]	1.098	1.091(21)	1.0791(3)	1.0776	1.0776
C–C=C	107.5(2)		107.8(1)	107.8(1)		107.7(10)[f]	107.90(1)	108.25	108.02
O=C–C	128.8(2)		129.2(2)	129.2(2)		129.3(20)	129.61(1)	129.91	129.68
C=C–H	130.6(30)		129.7[g]	129.7[g]		128.9(33)	129.99(0)	129.71	129.69
O–C–C	108.5(2)[f]		108.3(1)[f]	108.2(1)[f]		108.8(12)	108.07(0)	107.44	107.84
C–O–C	108.0(2)[f]		107.8(1)[f]	107.9(1)[f]		107.0(11)	108.06(1)	108.62	108.28
O=C–O	122.7(2)[f]		122.5(1)[f]	122.6(1)[f]		121.9(12)[f]	122.32(1)	122.65	122.49
R_f,%[h]	3.6		3.5	3.5		4.2			

[a] Bond length in angstroms and bond angles in degrees with three times the estimated standard errors in parentheses.
[b] Ref. [1].
[c] Ref. [2].
[d] With aug-cc-pVTZ basis set.
[e] Refined in one group. Difference between parameters in the group was assumed at the value from the MP2/aug-cc-pVTZ calculation.
[f] Dependent parameter.
[g] Assumed at the value from MP2/aug-cc-pVTZ calculation.
[h] Total disagreement factor.