

(br, 1 H), 7.20-7.66 (m, 5 H). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.59; H, 6.53; N, 5.29.

Synthesis of *N*-Benzoyltryptophan Methyl Ester (42). This compound was synthesized by procedures similar to the preparation of **39** from **18**: 74% yield; mp 110.8-112.5 °C (from AcOEt:hexane); IR (KBr) 3360, 1730, 1635, 1512, 1302, 1240, 1015, 732 cm^{-1} ; NMR ($CDCl_3$) δ 3.35 (d, $J = 6.0$ Hz, 2 H), 3.59 (s, 3 H), 5.04 (m, 1 H), 6.67-7.78 (m, 11 H), 8.90 (br, 1 H). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.73; H, 5.57; N, 8.55.

Synthesis of *N*-[(4-Methylphenyl)sulfonyl]tryptophan Methyl Ester (43). This compound was also prepared as follows. A solution of **20** (0.626 g, 2 mmol) and phenylhydrazine hydrogen chloride (0.3 g, 2.1 mmol) in glacial acetic acid (10 mL) was heated at 100 °C for 4 h under nitrogen atmosphere. After the solution was cooled, brine (20 mL) was added, and the organic portion was extracted with CH_2Cl_2 (20 mL \times 3). The extract was washed with brine and aqueous $NaHCO_3$ (20 mL). The organic layer was dried on $MgSO_4$, which was then filtered off. After the solvent was removed in vacuo, the residue was column chromatographed on silica gel (AcOEt:hexane 1:1) to afford **43** (0.54 g): 73% yield; mp 128.5-130.0 °C (from methanol); IR (KBr) 3404, 3290, 3055, 2950, 1742, 1350, 1168, 1100, 747, 680 cm^{-1} ; NMR ($CDCl_3 + Me_2SO-d_6$) δ 2.36 (s, 3 H), 3.14 (d, $J = 8.0$ Hz, 2 H), 3.46 (s, 3 H), 4.00-4.30 (m, 1 H), 6.77-7.23 (m, 5 H), 7.27-7.67 (m, 4 H), 9.9 (br, 1 H). Anal. Calcd for $C_{19}H_{20}N_2O_4S$: C, 61.27; H, 5.41; N, 7.52; S, 8.61. Found: C, 61.41; H, 5.38; N, 7.63; S, 8.43.

Transformation of *N*-Benzoyltryptophan Methyl Ester (42) to Tryptophan. Acid-catalyzed hydrolysis of **42** resulted in the formation of many unidentified products. On the other hand, the hydrolysis of **42** under alkaline conditions gave tryptophan **44**. A solution of **42** (3 g, 9.3 mmol) in 50% aqueous KOH (15 mL) was refluxed for 12 h. After the solution was cooled, the precipitate was filtered off and the solid was washed with water. The combined aqueous solution was acidified to pH 6 with concentrated HCl. After 1 h, the precipitate was filtered, washed with 30% aqueous EtOH (3 mL), EtOH (5 mL), and CH_2Cl_2 (20 mL), successively. The crude tryptophan was again dissolved in water (5 mL) containing a small amount of NaOH (0.5 g), and ethanol (10 mL) was added into the solution to precipitate a white solid, which was filtered off. The filtrate was warmed to 70 °C and acidified to pH 6 with acetic acid. Tryptophan was isolated as a plate crystal by cooling the above solution; 1.32 g (6.47 mmol), 70% yield. The IR spectrum of tryptophan was identical with that of DL-tryptophan **44**.

Synthesis of L-Tryptophan 45 from 43.⁵ A solution of **43**

(1.89 g, 5 mmol) and Me_4NCl (1.1 g, 10 mmol) in methanol (25 mL) was placed in a cathodic side of a divided cell equipped with a platinum anode and a lead cathode, and a solution of Me_4NCl (0.5 g, 4.56 mmol) in methanol (25 mL) was placed in the anodic side. A constant current (0.3 A, 4 A/dm²) was passed through the cell for 1.5 h, and then further electricity (0.15 A, 50 min) was passed. During the electrolysis, a methanolic solution saturated with HCl (0.4 mL) was gradually added into the catholyte.

After the reduction, the catholyte was neutralized, and the solvent was evaporated in vacuo to afford a residue. The residue was then dissolved in water, and 2 N sodium hydroxide was added to make the solution alkaline (pH 10). Amino ester was extracted with CH_2Cl_2 (20 mL \times 4) and dried on $MgSO_4$. The drying agent was filtered off and the evaporation of solvent gave a residue which was dissolved in 33% EtOH-water (15 mL) containing NaOH (0.27 g). The solution was stirred at room temperature overnight. Then, the solution was neutralized with 20% HCl to yield a precipitate, which was isolated by filtration and washed with EtOH (1 mL \times 5). The IR spectra of this precipitate was identical with that of authentic tryptophan. The optical rotation of this precipitate was 95% of that of authentic tryptophan; 52% yield.

Oxidation Potentials. Oxidation peak potentials were measured at room temperature by using an H-type cell, potentiostat H-type cell, potentiostat HA-104, and Function Generator HB-107A (Hokuto Denko Ltd.). Oxidation was carried out in dry acetonitrile containing 0.1 M $LiClO_4$ as a supporting electrolyte at platinum electrode using on aqueous saturated calomel reference electrode. The scan rate was 100 mV/s. The concentration of substrates and the values of peak potentials were shown in Table I.

Acknowledgment. One of the authors (Y.M.) wishes to thank the Ministry of Education, Science, and Culture, Japan for the Grant-in-Aid for Scientific Research (B) (No. 57470066).

Registry No. **5**, 618-42-8; **6**, 1796-27-6; **7**, 4703-22-4; **8**, 3989-48-8; **9**, 4972-36-5; **10**, 13041-25-3; **11**, 37097-43-1; **12**, 2404-03-7; **14**, 67488-65-7; **17**, 50353-17-8; **18**, 86658-76-6; **19**, 91411-07-3; *cis*-**20**, 91464-60-7; *trans*-**20**, 91464-62-9; **21**, 91411-08-4; **22**, 91411-09-5; **23**, 91411-18-6; **24**, 91411-10-8; **25**, 91411-11-9; **26**, 53279-96-2; **27**, 91411-12-0; **30**, 13735-81-4; **31**, 91411-15-3; **32**, 91411-13-1; **33**, 91411-14-2; **34**, 91411-19-7; **35**, 91411-17-5; **36**, 91411-16-4; **39**, 86658-78-8; **40**, 5493-38-9; *cis*-**41**, 91464-61-8; *trans*-**41**, 91464-63-0; **42**, 2717-75-1; **43**, 79659-73-7; **44**, 54-12-6; **45**, 73-22-3; $P(OCH_3)_3$, 121-45-9.

Photoelectron Spectra of Dioxabicyclo[*n*.2.1]alkanes

Rolf Gleiter,* Walter Dobler, and Mirjana Eckert-Maksić

Organisch-Chemisches Institut der Universität, Heidelberg, D-6900 Heidelberg, West Germany

A. John Bloodworth and Henny J. Eggelte

Department of Chemistry, University College, London, London, WC1H 0AJ, Great Britain

Dieter Cremer

Lehrstuhl für Theoretische Chemie der Universität, Köln, D-5000 Köln, West Germany

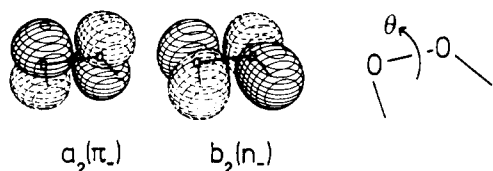
Received April 5, 1984

The He(I) photoelectron (PE) spectra of 7-bromo-2,3-dioxabicyclo[2.2.1]heptane (**1a**), 8-bromo-6,7-dioxabicyclo[3.2.1]octane (**2a**), 9-bromo-7,8-dioxabicyclo[4.2.1]nonane (**3a**), 10-bromo-8,9-dioxabicyclo[5.2.1]decane (**4a**), and the corresponding unsubstituted bicyclic peroxides **2b-4b** have been recorded. The assignment of the PE spectra of **1-4** is made empirically and on the basis of model calculations (MINDO/3 and MNDO) for **1b-4b** and ab initio for **1b** and **2b**. For **2** we find that one σ -level is placed between π_- and n_- . A comment is made on the relationship between the split of the bands assigned to π_- and n_- and the C-O-O-C torsional angle θ .

Recently the He(I) photoelectron (PE) spectra of a number of cyclic and bicyclic peroxides have been re-

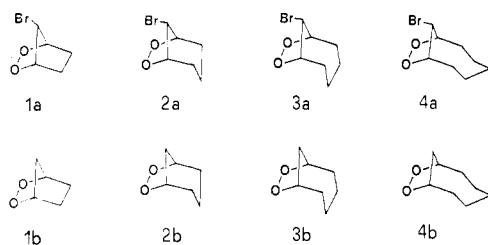
ported.¹⁻⁵ For the bands which were assigned as due to ionization events from $a_2(\pi_-)$ and $b_2(n_-)$, a correlation with

the C-O-O-C dihedral angle θ was found.



While Coughlin et al.² favor a linear relationship between $\Delta I = I_v(n_-) - I_v(\pi_-)$ and θ , Rademacher³ as well as Gleiter and Bloodworth et al.⁴ advocate a linear relationship between ΔI and $\cos \theta$. This discrepancy was ascribed by us as being due to the uncertainty in the estimation of the dihedral angle for dioxolane, and microwave and ab initio studies⁵ have since vindicated this view.

To contribute further to this discussion, we have recorded the PE spectra of seven recently synthesized⁶ dioxabicyclo[n.2.1]alkanes, the bromo peroxides **1a–4a** and the parent compounds **2b–4b**.



The peroxides **2a–4a** were investigated because their X-ray structures have recently been solved⁷ and so the dihedral angles θ at the peroxy group are known. For 1 a θ value of 0° can be assumed safely.

Figure 1 shows four representative PE spectra, namely, those of compounds **1a**, **2a**, **2b**, and **3b**. The PE spectra of the bromo compounds **1a** to **4a** are similar in so far as they show one band at low energy (below 10 eV) followed by two close-lying sharp peaks between 10.3 and 10.6 eV. The two sharp peaks are not present in the parent compounds. For 1–3 it is possible to single out one or two further bands at energies above 10.6 eV. In Table I the recorded vertical ionization energies of the first bands of all eight compounds are listed.

Assignment of the Spectra

To assign the bands we have proceeded in two ways. First, we have used an empirical approach, comparing the spectra with those of related compounds and making use of a simple assumption concerning the relationship between the C-O-O-C dihedral angle θ and the split ΔI between π_- and n_- . Second, we have referred to the results of the theoretical calculations using Koopmans' theorem.⁸

Table I. Experimentally Determined Vertical Ionization Energies in eV for 1–4 Together with the Assignment

compd	band	$I_{v,j}$	assignment
1a	1	9.3	π_-
	2	10.33	4p
	3	10.62	
	4	11.5	
1b	1	8.96	π_-
	2	11.26	n_-
2a	1	9.3	π_-
	2	10.3	4p
	3	10.6	
	4	10.8	
	5	11.6	n_-
2b	1	9.05	π_-
	2	10.6	σ
	3	11.3	n_-
3a	1	9.2	π_-
	2	10.3	4p
	3	10.6	
	4	11.0	
	5	11.6	σ
3b	1	8.9	π_-
	2	10.6	n_-
	3	11.3	σ
4a	1	9.6	π_-
	2	10.3	4p
	3	10.5	
	4	10.8	
4b	1	9.2	π_-
	2	10.4	n_-

In this latter approximation it is assumed that the measured vertical ionization energy, $I_{v,j}$, can be set equal to the negative value of the orbital energy ($-\epsilon_j$) calculated for the ground state of the neutral molecule. The assumption we have made concerning the relationship between ΔI and the dihedral angle θ of the peroxy moiety is that for θ values of around 0° , ΔI values of between 2.2 and 2.4 eV are to be expected. From the results gathered so far,^{1–5} this assumption seems to be the only safe one.

(a) **Empirical Assignment.** If we assign the recorded bands of the spectra of **1a** to **4a** empirically, we come up with the following suggestion. Band 1 of all four compounds is due to ejection of electrons from the π_- MO, while bands 2 and 3 are due to ionization from the two 4p lone pair orbitals localized on the Br substituent. The latter assignment is confirmed by the following observations: (i) these bands (10.3–10.6 eV) remain essentially constant through **1a** to **4a**, (ii) both bands are absent in the parent compounds, and (iii) other bromohydrocarbons show similar ionization energies with two sharp bands split by 0.3 eV.⁹

If we compare the energies of the π_- bands of **1a–4a** with those of **1b–4b** (Table I), we encounter a shift toward lower energies by 0.2–0.3 eV in the unsubstituted peroxides. This observation is due to the inductive effect of the halogens.

In the case of **1a** we expect a split of at least 2.2 eV between π_- and n_- according to our assumption. We therefore assign band 4 in the PE spectrum of **1a** to the ionization from n_- . In line with this are also the assignments given for **1b**.^{2,4}

For the PE spectra of **2a** and **2b**, we again expect a split of 2.2–2.4 eV between π_- and n_- according to our assumption because the C-O-O-C dihedral angle in **2a** has been measured as 0° .⁷ This points to band 5 in the spectrum of **2a** and band 3 in that of **2b** for the assignment to n_- . We assign band 4 in **2a** and band 2 in **2b** to ioni-

(1) Batich, C.; Adam, W. *Tetrahedron Lett.* 1974, 1467. Brown, R. S. *Can. J. Chem.* 1975, 53, 3469. Brown, R. S.; Marcinko, R. W. *J. Am. Chem. Soc.* 1978, 100, 5584. Kimura, K.; Osafune, K. *Bull. Chem. Soc. Jpn.* 1975, 48, 2421.

(2) Coughlin, D. J.; Brown, R. S.; Salomon, R. G. *J. Am. Chem. Soc.* 1979, 101, 1533.

(3) Rademacher, P.; Elling, W. *Liebigs Ann. Chem.* 1979, 1473.

(4) Gleiter, R.; Schang, P.; Adam, W.; Eggelte, H. J.; Erden, I.; Bloodworth, A. J. *J. Electron Spectrosc. Relat. Phenom.* 1980, 19, 223.

(5) Kondo, T.; Tanimoto, M.; Matsumoto, M.; Nomoto, K.; Achiba, Y.; Kimura, K. *Tetrahedron Lett.* 1980, 21, 1649. Cremer, D. *Isr. J. Chem.* 1983, 23, 72. Cremer, D. In "The Chemistry of Functional Groups, Peroxides"; Patai, S., Ed.; Wiley: New York, 1983; p 1.

(6) Bloodworth, A. J.; Eggelte, H. J. *J. Chem. Soc., Perkin Trans. 1* 1981, 1375; *J. Chem. Soc., Chem. Commun.* 1982, 865.

(7) Bloodworth, A. J.; Eggelte, H. J.; Galas, A. M. R.; Hursthouse, M. B.; Walker, N., to be published.

(8) Koopmans, T. *Physica (Amsterdam)* 1934, 1, 104.

(9) Hashmall, J. A.; Heilbronner, E. *Angew. Chem.* 1970, 82, 320; *Angew. Chem., Int. Ed. Engl.* 1970, 9, 305.

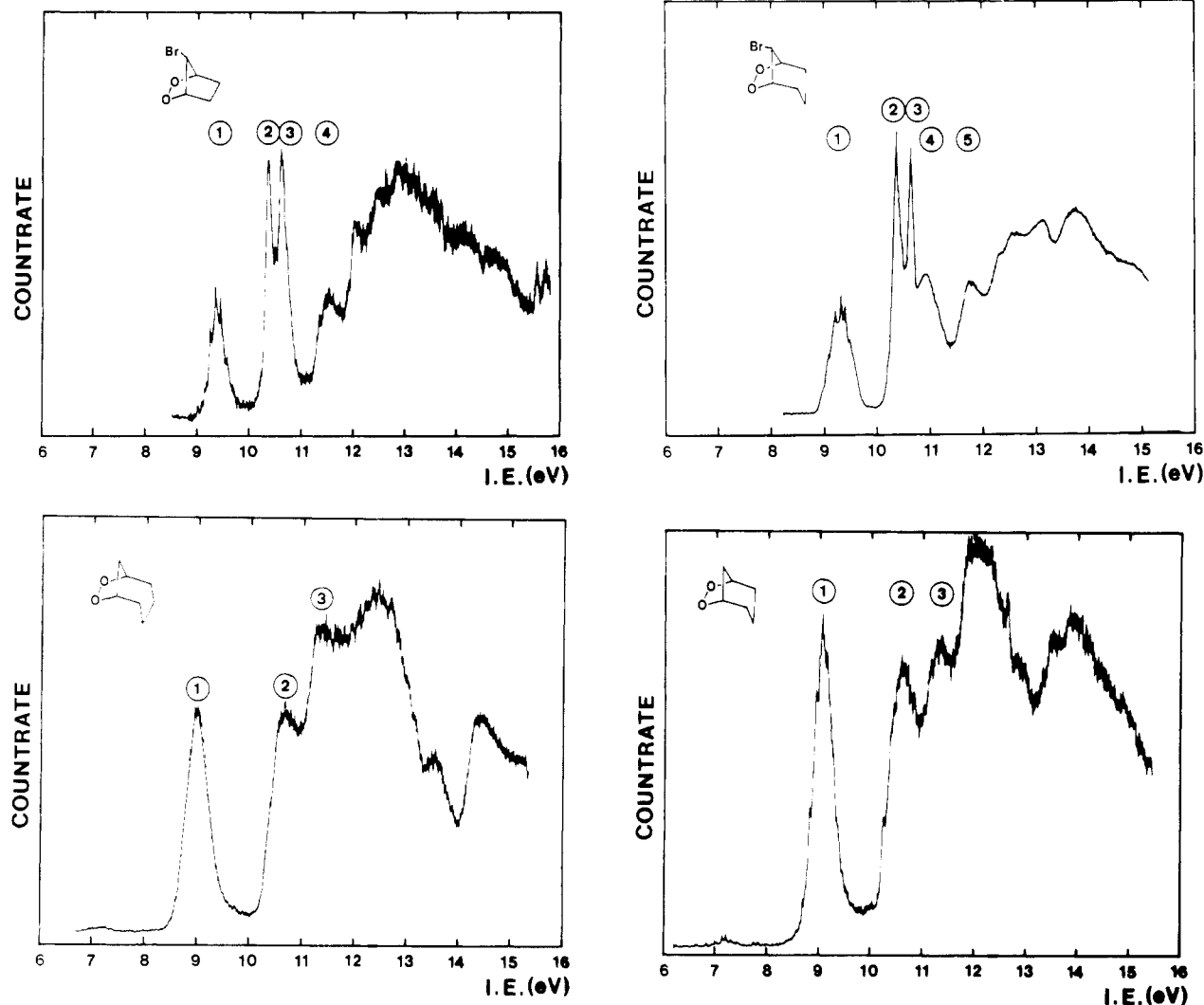


Figure 1. PE spectra of 1a, 2a, 2b, and 3b.

zation events from one or even two σ -orbitals.

For compounds 3 and 4, where dihedral angles of 14° and 44° , respectively, have been found,⁷ the split ΔI should be smaller than that for 1 and 2. Hence we assign band 4 in 3a and 4a and band 2 in 3b and 4b as originating from the ionization from n_- .

For 3a and 3b we also list in Table I bands 5 and 3, respectively, since these bands can be discriminated clearly from those at higher energy. We assign them to ionizations from σ -orbitals since the energy difference to band 1 is larger than 2.2 eV.

The assignments for 2 are somewhat unusual in that at least one high-lying σ -orbital is placed at higher energy than n_- . So far it has always been assumed a priori that, setting aside bands associated with additional π -bonds, lone pairs, etc., the second band in the PE spectra of cyclic and bicyclic peroxides is due to ionization out of the n_- orbital. Here we have an example where this does not seem to be so. Since in several cases the ΔI value between the first and second band has been used to estimate the dihedral angle at the peroxy group, this example might be considered as a warning.

In Figure 2 we have correlated the first bands in the PE spectra of 1a to 4a according to the empirical assignment just discussed.

(b) Model Calculations. To check our empirical assignment of the PE spectra of 1-4 and to understand the orbital sequence indicated for 2, we have carried out model calculations. We have used semiempirical methods

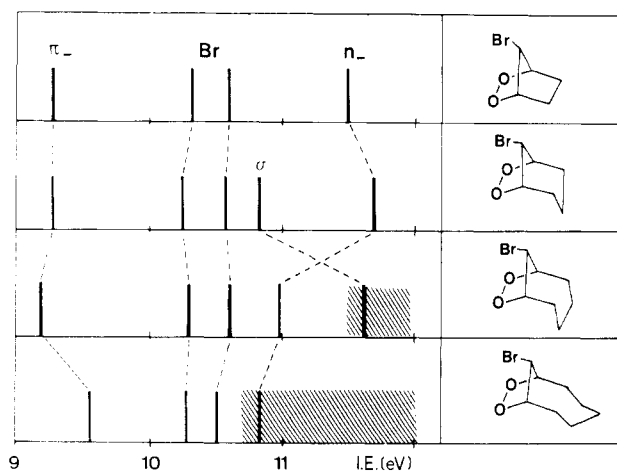


Figure 2. Correlation between the first four bands in the PE spectra of 1a to 4a.

(MINDO/3,¹⁰ MNDO¹¹) for 1b-4b and nonempirical restricted-Hartree-Fock (HF) theory employing a split va-

(10) Bingham, R.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285. Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

(11) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. Bischof, P.; Friedrich, G. *J. Comput. Chem.*, **1982**, *3*, 486.

(12) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(13) Langs, O. A.; Erman, M. G.; DeTitta, G. T.; Coughlin, D. J.; Salomon, R. G. *J. Cryst. Mol. Struct.* **1978**, *8*, 239.

Table II. Calculated Orbital Energies of 1b-4b Using the MINDO/3 and the MNDO Method. For 1b and 2b the Results of a Restricted HF Calculation Using a Split Valence (4-31G) Basis Have Been Added^a (All Values in eV)

compd	$-\epsilon_i$ (MINDO/3)	$-\epsilon_i$ (MNDO)	$-\epsilon_i$ (4-31G) ^a
1b	9.31 8a''(π_-)	10.42 8a''(π_-)	11.00 8a''(π_-)
	10.76 7a''(n ₋)	12.33 12a'(σ)	12.66 7a''(n ₋)
	10.94 12a'(σ)	12.43 7a''(n ₋)	12.97 12a'(σ)
2b	9.05 9a''(π_-)	10.58 9a''(π_-)	11.36 9a''(π_-)
	10.26 14a'(σ)	11.73 14a'(σ)	12.09 14a'(σ)
	10.47 8a''(σ)	12.07 8a''(σ)	12.18 8a''(σ)
	11.25 7a''(n ₋)	12.42 13a'(σ)	12.94 13a'(σ)
	11.27 13a'(σ)	12.95 7a''(n ₋)	13.46 7a''(n ₋)
	9.53 11a''(π_-)	10.51 11a''(π_-)	
3b	10.31 10a''(n ₋)	11.69 10a''(n ₋)	
	9.55 12a''(π_-)	10.51 12a''(π_-)	
4b	10.19 11a''(n ₋)	11.69 11a''(n ₋)	

^aOnly the valence orbitals are considered.

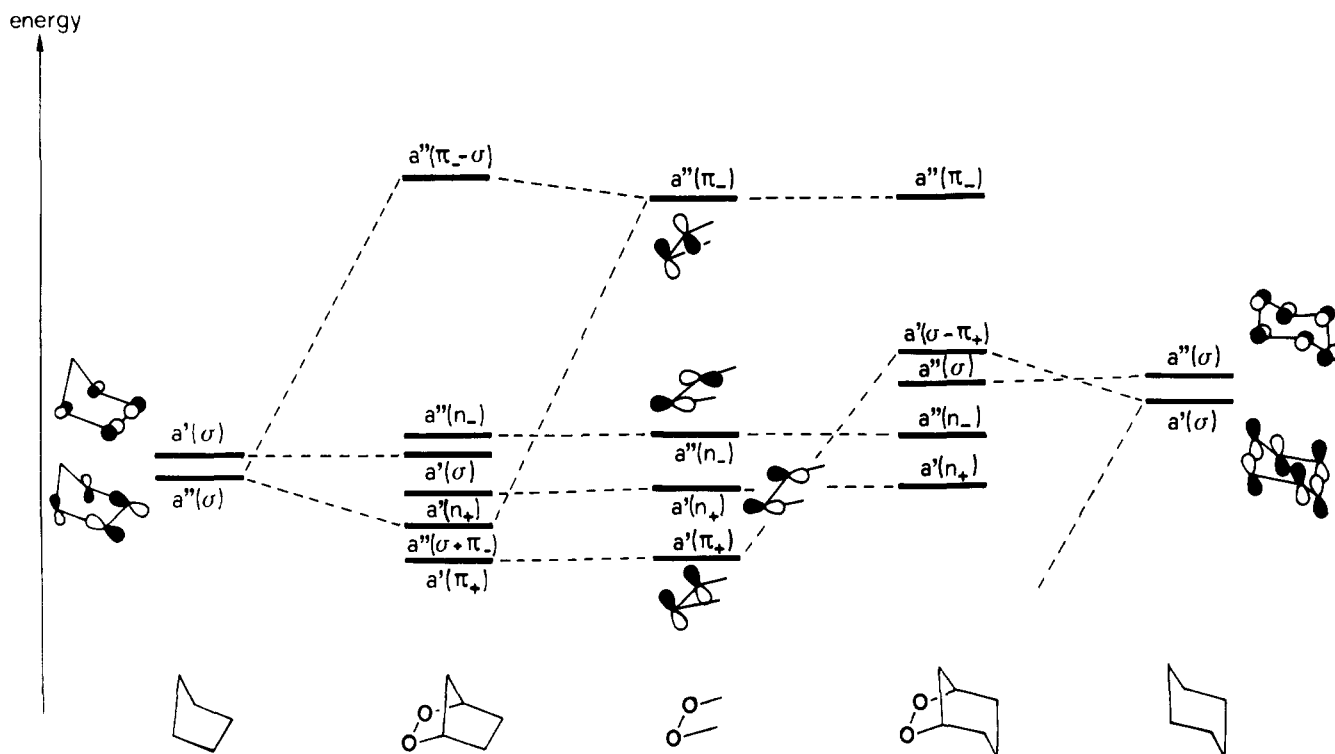


Figure 3. Qualitative interaction diagram between the highest occupied MO's of a peroxy group and those of a cycloalkane fragment. Only interactions with the two highest ribbon MO's a'' and a' of a six-membered (right) and five-membered ring (left) are shown. Note that the n_+ and n_- orbitals are almost orthogonal to the a' and $a''\sigma$ MO's and, therefore, do not interact.

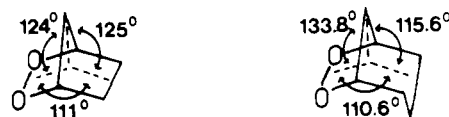
lence (4-31G) basis¹² for **1b** and **2b**.

In the case of the two semiempirical methods, we have minimized all geometrical parameters of **1b-4b**. The predicted O-O bond length of 1.4 Å found for all four species is too short by about 0.08 Å.^{5,14} The calculated orbital energies are given in Table II. It is seen that both semiempirical methods agree with our empirical assignment for **3b** and **4b**, since the orbital sequence predicted is $a''(\pi_-)$ on top of $a''(n_-)$, the latter orbital being heavily mixed with the σ -frame.

For **1b**, MINDO/3 predicts $8a''(\pi_-)$ on top of $7a''(n_-)$, while MNDO places a σ -orbital ($12a'$) between them. In the case of **2b**, MINDO/3 predicts two σ -orbitals ($14a'$ and $8a''$) and MNDO three σ -orbitals ($14a'$, $8a''$, and $13a'$) between $9a''(\pi_-)$ and $7a''(n_-)$.

To explore the electronic structure prevailing in **1b** and **2b** further, we used the restricted HF theory employing a 4-31G basis.¹² The geometrical parameters used were those obtained from the X-ray investigations on the 1,4-diphenyl derivative of **1b**¹³ and on **2a**.⁷ In both cases we

assumed C_s symmetry and C-H bond lengths of 1.09 Å. The dihedral angles adopted are shown below for **1b** and **2b**.



The results obtained for **1b** and **2b** are shown in Table II. The orbital sequence predicted for **1b** agrees with that calculated according to the MINDO/3 method, i.e., the orbitals $8a''$ and $7a''$ are placed on top of a σ -orbital ($12a'$).

In the case of **2b**, the ab initio calculation agrees with the sequence found by the MNDO method. However, shortening the O-O distance from 1.500 Å found by X-ray investigations on **2a** and **3a** to 1.475 Å found by microwave investigations on the ozonide of cyclopentene¹⁴ results in the energy of $7a''(n_-)$ being raised while that of $13a'(\sigma)$ is lowered. It is likely that the two MO's cross provided the geometry is fully relaxed. In this case the sequence found by the ab initio calculations parallels that obtained by the MINDO/3 method.

(14) Borseth, D. G.; Kuczkowski, R. L. *J. Phys. Chem.* 1983, 87, 5381.

Table III. Correlation between Experimentally Determined Dihedral Angle θ and ΔI for Cyclic and Bicyclic Peroxides

compd	θ , deg (ref)	ΔI	(ref)
2a	0-2 (7)	2.3	a
3a	14 \pm 2 (7)	1.8	a
4a	44 \pm 2 (7)	1.2	a
5	50 \pm 2° (5)	1.27	2
6	80 \pm 2° (5)	<0.4	5

^aThis work.

Discussion

Since a rigorous geometry optimization at the 4-31G level was not undertaken, the results remain qualitative in character. Nevertheless the calculations help us to understand the electronic structure of **2b**.

The sequence of the highest occupied MO's of **1b** and **2b** can be derived by a simplified perturbation treatment including the highest occupied MO's of the peroxy group (π_- , n_- , n_+ , π_+) shown in the center of Figure 3 and those of the cyclopentane (left) and cyclohexane fragment (right). Note that the basis orbital energies of the five-membered rings are lower than those of six-membered ring. The main interaction encountered between the ribbon orbitals of the six-membered ring¹⁵ and the peroxy group is that between $a'(\sigma)$ and $a'(\pi_+)$, which leads to a destabilization of the ribbon orbital. In the case of the five-membered ring fragment, $a''(\sigma)$ interacts with $a''(\pi_-)$ and thus enlarges the gap between $a''(\pi_- - \sigma)$ and $a''(n_-)$. The n_+ and n_- MO's of the peroxy moiety do not interact with the ribbon orbitals of proper symmetry of both rings since σ - and n -orbitals are orthogonal to each other.

(15) Hoffmann, R.; Mollère, P. D.; Heilbronner, E. *J. Am. Chem. Soc.* 1973, 95, 4860.

To provide a firm basis for clarifying the nature of the relationship between the C-O-O-C dihedral angle (θ) and the split (ΔI) of bands in the PE spectrum assigned to ionizations from n_- and π_- , it is essential to measure PE spectra of peroxides for which the dihedral angle has been determined experimentally. The measured ΔI and experimentally determined θ for **2a-4a** are listed in Table III together with similar data for the two monocyclic peroxides **5** and **6** which, as far as we are aware, are the



only other peroxides for which such information is available. Although a considerable step forward, these data are not yet sufficient to decide whether a $\Delta I/\theta$ or a $\Delta I/(\cos \theta)$ correlation should be used.

Experimental Section

The preparation of the peroxides has been reported elsewhere.⁶ The PE spectra of the pure samples were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer equipped with a He(I) source. All spectra were recorded at room temperature and were calibrated with xenon and argon. A resolution of ± 0.05 eV was achieved for the single bands and of ± 0.1 eV for the shoulders.

Acknowledgment. R.G., W.D., M.E.-M., and D.C. are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the A. von Humboldt Foundation, and A.J.B. and H.J.E. thank the Science and Engineering Research Council for financial support.

Registry No. **1a**, 72536-23-3; **1b**, 279-35-6; **2a**, 78535-39-4; **2b**, 51272-66-3; **3a**, 78521-95-6; **3b**, 68525-35-9; **4a**, 71245-79-9; **4b**, 69492-24-6.

Formation of Olefins from Alkyl Radicals with Leaving Groups in the β -Position

Manfred K. Eberhardt

Puerto Rico Cancer Center, University of Puerto Rico, Medical Sciences Campus, San Juan, Puerto Rico 00936

Received January 18, 1984

A reaction of ethanol with Fe^{2+} -ethylenediaminetetraacetate (EDTA)- O_2 to give ethylene is described. This olefin-forming reaction was observed with a wide variety of compounds (alcohols, halides, ethers, acetates, ethyl sulfide, and *N,N*-diethylaniline). Olefins were also produced with Cu^+ - O_2 in acidic solution and Fe^{2+} -EDTA- H_2O_2 and in some cases with Fe^{2+} - H_2O_2 . The effect of H^+ , H_2O_2 , EDTA, Fe^{2+} , and O_2 concentrations on olefin formation was investigated. A mechanism involving formation of a β -substituted radical, followed by a simultaneous electron transfer and elimination of the leaving group (reductive elimination) is proposed.

In connection with work on the mechanism of the Fe^{2+} -ethylenediaminetetraacetate (EDTA)- O_2 hydroxylating system we have observed the formation of ethylene in the presence of ethanol. This olefin-forming reaction was found to occur with a wide variety of compounds (alcohols, halides, ethers, acetate, ethyl sulfide, and *N,N*-diethylaniline). Olefins were also produced with Cu^+ - O_2 ¹ in acidic solution and with Fe^{2+} -EDTA- H_2O_2 and in some cases with Fe^{2+} - H_2O_2 . In this paper we present the results

of these studies and a discussion of the mechanism of this radical induced formation of olefins.

Results and Discussion

We have studied the effect of Fe^{2+} , EDTA, and O_2 concentration on the formation of isobutylene from *tert*-butyl alcohol. These results are shown in Table I. The highest yield of isobutylene was obtained with equal amounts of Fe^{2+} and EDTA (10^{-2} M) and in air-saturated aqueous solutions. If the reaction was carried out in oxygen-saturated solution (10^{-3} M) or in argon saturated (deoxygenated) solution the yield of isobutylene decreased considerably. The small amount of isobutylene (25×10^{-6}

(1) In a similar system (Cu^{2+} -ascorbic acid) the formation of ethylene from ethanol and ethyl ether was noted by Lieberman and Mapson (Lieberman, M.; Mapson, L. W. *Nature (London)* 1964, 204, 343).