pathway involving nitrosobenzene "chain carrier" (eq 3).

The nitroso oxide is thus shown to behave as an electrophilic peroxy radical **1b** and isomerize according to eq 2. These are in sharp contrast to the case of carbonyl oxides that are well pictured as dipolar **1a**. There is no evidence for the cyclization of carbonyl oxides (e.g., **1** → **2**);[14] a high energy barrier for the cyclization is certainly due to the double-bond character of the C–O bond in **1a**.[15] In contrast, the cyclization of nitroso oxides appears to be facile because of the diradical character of structure **1b**, reflecting diminished importance of double-bond nature in N–O. An extended ab initio MO calculation has suggested that most important is dipolar **1a** for carbonyl oxides but diradical **1b** for nitroso oxides.[16] Our experimental results are consistent with the prediction. The structural weights (i.e., **1a**, **1b**, or **2**) and reactivities of XOO species are considered to be controlled by the difference in electronegativities between X and oxygen atom. This point is currently under invesigation.

Registry No. (p-MeOC$_6$H$_4$)$_2$SO, 1774-36-3; (p-MeC$_6$H$_4$)$_2$SO, 1774-35-2; Ph$_2$SO, 945-51-7; (p-ClC$_6$H$_4$)$_2$SO, 3085-42-5; (p-MeC$_6$H$_4$)$_2$S, 620-94-0; Ph$_2$S, 139-66-2; (p-ClC$_6$H$_4$)$_2$S, 5181-10-2; PhNOO, 105785-77-1; PhN$_3$, 622-37-7.

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(14) (a) Ishiguro, K.; Tomizawa, K.; Sawaki, Y.; Iwamura, H. *Tetrahedron Lett.* **1985**, *26*, 3723. (b) Ishiguro, K.; Hirano, Y.; Sawaki, Y., unpublished results.

(15) Hull, L. A. *J. Org. Chem.* **1978**, *43*, 2780.

(16) Hiberty, P. C.; Ohanessian, G. *J. Am. Chem. Soc.* **1982**, *104*, 66.

Femtosecond Photochemical Ring Opening Dynamics of 1,3-Cyclohexadiene from Resonance Raman Intensities[1]

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Photoexcitation to the lowest allowed singlet state of 1,3-cyclohexadiene (CHD) gives rise to efficient ring opening to *all-cis*-hexatriene whose stereochemistry, as measured by product analysis[2] is overwhelmingly conrotatory, in accordance with the Woodward–Hoffmann rules.[3] Due to the diffuseness of the electronic spectrum,[4] the paucity of luminescence,[5] and the exceedingly short excited-state lifetime,[6] direct measurements of the excited-state structure and dynamics of CHD have not been performed. The existence of barriers to ring opening, the lifetime and extent of geometry change on the initially prepared excited-state surface, the degree of concertedness, and the participation of diradical or zwitterionic intermediates have remained unknown.[7] The quantitative analysis of resonance Raman intensities provides a powerful new method for examining excited-state structure and dynamics,[8,9] which we apply here to cyclohexadiene. The resonance enhancement of the 1321-cm^{-1} symmetric CH$_2$ wag and the 948-cm^{-1} CH$_2$–CH$_2$ stretch reveals that the regio- and stereochemical preference predicted by the Woodward–Hoffmann rules is established within the first 20 fs following excitation via specific, rapid evolution along the conrotatory ring opening reaction coordinate.

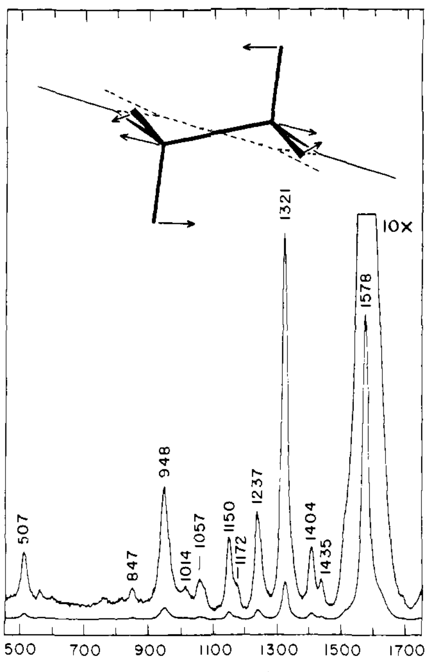

Figure 1. Resonance Raman spectrum of flowing neat cyclohexadiene excited with a D$_2$-shifted Nd:YAG laser at 292.6 nm (100 μJ/pulse, 20 Hz). The detection system consisted of an intensified reticon array coupled to a spectrograph having a slit width of 6 cm^{-1}. The inset depicts the ground-state geometry of cyclohexadiene, and the arrows give the geometry changes that occur along the 948 and 1321 cm^{-1} normal modes 20 fs after excitation (multiplied by ~10). Motions of the diene moiety have been suppressed for clarity.

The resonance Raman intensity of a vibration is determined primarily by the slope of the excited-state potential surface along that normal coordinate at the vertically excited geometry. Rapid photochemical dynamics are thus reflected by intense resonance Raman scattering by any normal modes having large projections onto the reactive coordinates.[8,9] In our analysis, the excited state is treated as a harmonic potential characterized by a vertical excitation energy E_0 and a dimensionless origin shift Δ along each totally symmetric normal coordinate. The set of displacements is defined by the relative resonance Raman intensities and by the width of the electronic absorption envelope. The total absolute resonance Raman cross section permits an experimental partitioning of the total vibronic line width into homogeneous and

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(1) This research was supported by the National Science Foundation (CHE 81-16042).

(2) (a) de Kock, R. J.; Minnaard, N. G.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 922. (b) Baldwin, J. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1969**, *91*, 6444. (c) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285. (d) Spangler, C. W.; Hennis, R. P. *J. Chem. Soc., Chem. Commun* **1972**, 24.

(3) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17.

(4) Minnaard, N. G.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1179.

(5) Fluorescence has been observed for steroidal cyclohexadienes which are rigid (Havinga, E.; de Kock, R. J.; Rappoldt, M. P. *Tetrahedron* **1960**, *11*, 276) but not for CHD itself (de Kock, R. J. Ph.D. Thesis, University of Leiden, 1959).

(6) Gottfried, N.; Kaiser, W.; Braun, M.; Fuss, W.; Kompa, K. L. *Chem. Phys. Lett.* **1984**, *110*, 335.

(7) (a) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305. (b) Dauben, W. G.; McInnis, E. L.; Michno, D. M. *Org. Chem.* (*N. Y.*) **1980**, *3*, 91.

(8) (a) Myers, A. B.; Mathies, R. A. In *Biological Applications of Raman Spectroscopy*; Spiro, T. G., Ed., Wiley-Interscience: New York, in press. (b) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822. (c) Champion, P. M.; Albrecht, A. C. *Annu. Rev. Phys. Chem.* **1982**, *33*, 353. (d) Warshel, A.; Dauber, P. *J. Chem. Phys.* **1977**, *66*, 5477. (e) Chadwick, R. R.; Gerrity, D. P.; Hudson, B. S. *Chem. Phys. Lett.* **1985**, *115*, 24. (f) Patapoff, T. W.; Turpin, P.-Y.; Peticolas, W. L. *J. Phys. Chem.* **1986**, *90*, 2347. (g) Morris, D. E.; Woodruff, W. H. *J. Phys. Chem.* **1985**, *89*, 5795. (h) Sue, J.; Yan, Y. J.; Mukamel, S. *J. Chem. Phys.* **1986**, *85*, 462. (i) Ziegler, L. D.; Varotsis, C. *Chem. Phys. Lett.* **1986**, *123*, 175. (j) Hale, M. O.; Galica, G. E.; Glogover, S. G.; Kinsey, J. L. *J. Phys. Chem.* **1986**, *90*, 4997.

(9) (a) Myers, A. B.; Mathies, R. A.; Tannor, D. J.; Heller, E. J. *J. Chem. Phys.* **1982**, *77*, 3857. (b) Myers, A. B.; Harris, R. A.; Mathies, R. A. *J. Chem. Phys.* **1983**, *79*, 603. (c) Myers, A. B.; Mathies, R. A. *J. Chem. Phys.* **1984**, *81*, 1552. (d) Myers, A. B.; Trulson, M. O.; Mathies, R. A. *J. Chem. Phys.* **1985**, *83*, 5000. (e) Myers, A. B.; Trulson, M. O.; Pardoen, J. A.; Heeremans, C.; Lugtenburg, J.; Mathies, R. A. *J. Chem. Phys.* **1986**, *84*, 633.

0002-7863/87/1509-0586$01.50/0

inhomogeneous components.[9,10]

Resonance Raman spectra of CHD were obtained with excitation at 252, 266, 274, 282, and 292 nm. The absorption spectrum and Raman excitation profiles were calculated by using time-dependent wavepacket propagation techniques, and the set of excited-state parameters was adjusted to achieve the best agreement with experiment by using the methods we have described earlier.[8a,9] The final excited state Δ's and line widths are summarized in ref 11. Especially notable is the large homogeneous line width of 900 cm^{-1}, which corresponds to a relaxation time of ~10 fs.

Shown in Figure 1 is the Raman spectrum of CHD excited at 292.6 nm, ~500 cm^{-1} above the onset of absorption. The initial dynamics of the photoexcited molecule can be read directly from the spectrum: the ethylenic bond order inversion and flattening from C_2 symmetry to C_{2v} are evidenced by intensity in the 1578 cm^{-1} C=C stretch ($\Delta = 1.7$) and 507 cm^{-1} C=C—C=C torsion ($\Delta = 0.5$). The prominent 1321-cm^{-1} line ($\Delta = 0.8$) has been assigned as a totally symmetric (A species) wagging of the axial methylene hydrogens about an axis parallel to the C_2 symmetry axis.[12] The 948 cm^{-1} CH_2–CH_2 stretch shows a significant Δ of 0.4. Both of these modes are major components of the conrotatory ring opening reaction coordinate. The absence of B species CH_2 wag overtone intensity (data not shown) precludes any initial motion toward a pentadienyl-methylene geometry.[13] Rapid concerted methylene CH bond rehybridization toward the shorter sp^2 C–H equilibrium geometry is ruled out by the absence of methylene CH stretching intensity near 2950 cm^{-1}. It is evident that excitation to the lowest allowed electronic state of CHD induces rapid barrierless motion on a trajectory toward the geometry of *all-cis*-hextriene.

An explicit picture of the geometry changes that occur in CHD after electronic excitation can be generated by propagating a wavepacket on the experimentally derived excited-state surface. The arrows in Figure 1 present a superposition of the atomic displacements that occur along the 948- and 1321-cm^{-1} modes. The scissile C–C bond length increases by 0.1 Å and the axial CH bonds rotate 10° toward the molecular pseudoplane in the first 20 fs.[14] This observation is conclusive evidence of participation of the CH_2–CH_2 group in this nominal $\pi \rightarrow \pi^*$ excitation.

In summary, this is the first direct experimental observation, to our knowledge, of the early stages of any pericyclic rearrangement. *The unique aspect of this approach is that it permits the quantitation of mode-specific, ultrafast chemical dynamics without resorting to time-resolved measurements.* This work, which is being extended to include cyclobutene and cyclooctatriene, provides new data which can be used to critically evaluate theoretical calculations of excited-state potential surfaces for pericyclic rearrangements.

Acknowledgment. We are indebted to Prof. Johan Lugtenburg for discussions that led to this study and to Prof. W. G. Dauben for helpful discussions and encouragement.

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(10) (a) Grundherr, Chr. v.; Stockburger, M. *Chem. Phys. Lett.* **1973**, *22*, 253. (b) Schomacker, K. T.; Champion, P. M. *J. Chem. Phys.* **1986**, *84*, 5314.

(11) Trulson, M. O.; Dollinger, G. D.; Mathies, R. A. manuscript in preparation. Briefly, the final simulation was performed with an E_0 of 35 800 cm^{-1}, homogeneous half-width at half-maximum of 900 cm^{-1}, an electronic transition length of 0.65 Å, and displaced normal modes corresponding to the 12 strongest fundamentals (507 cm^{-1}, $\Delta = 0.54$; 557, 0.37; 750, 0.25; 948, 0.38; 1014, 0.25; 1057, 0.24; 1150, 0.35; 1237, 0.37; 1321, 0.82; 1404, 0.20; 1435, 0.09; 1578, 1.72).

(12) Normal mode assignments taken from: Di Lauro, C.; Neto, N.; Califano, S. *J. Mol. Struct.* **1969**, *3*, 219.) Those calculated in this laboratory by the QCFF/pi method, as outlined in Warshel et al. (Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5612) are in qualitative agreement. However, following Carreira et al. (Carreira, L. A.; Carter, R. O.; Durig, J. R. *J. Phys. Chem.* **1973**, *59*, 812) we assign the ring breathing mode at 847 cm^{-1} and the CH_2–CH_2 stretch at 948 cm^{-1}.

(13) B species fundamental scattering is forbidden if the ground electronic state maintains C_2 symmetry. The pentadienyl-methylene structure is generated by simultaneous evolution along A and B species twist coordinates, which would give rise to B twist overtone scattering.

(14) The conversion from dimensionless Δ values to internal coordinate displacements δ in Å or radians may be found in ref 8a.

Redetermination of the Experimental Electron Deformation Density of Benzenetricarbonylchromium

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Recently Kok and Hall[1] reported a theoretical calculation of the deformation density of benzenetricarbonylchromium which was at variance with previous experimental studies,[2,3] particularly in the region close to the metal. Stimulated by this discrepancy, we redetermined the electron density distribution in the molecule using the X–X method.[4] In contrast to the previous experimental work, we find positions for the maxima around the chromium atom that are close to those in the theoretical calculations. The results indicate, however, that the C_{3v} symmetry assumed in the theoretical calculations is a poor approximation for the symmetry of the molecule in the crystal and that a small distortion in the geometry of a transition-metal complex in a crystal can have a significant effect on the electron deformation density around the metal.

X-ray diffraction data were collected to a $\sin\theta/\lambda = 1.0$ Å^{-1} by using Mo Kα X-radiation. Experimental details are summarized in ref 5; more detailed information has been deposited. Data collection differed from that in previous studies in two important aspects. First, each reflection was multiply measured around the scattering vector (ψ scans), and, second, the strongest reflections were measured with a lower incident X-ray intensity and rescaled. A total of 16444 intensities were measured. Equivalent reflections were averaged to give 2590 independent reflections ($R_{av} = 0.01$). Only those reflections with $I > 2.0\sigma(I)$ (2484 reflections) were used for calculation of the electron deformation density.[5]

The electron deformation density in this study agrees well with the theoretical results of Kok and Hall, at least in the sections that are available to us.[1] Figure 1 shows a comparison of the theoretical and present experimental electron deformation density in the plane of the chromium atom, one carbonyl group, and the center of the benzene ring. Four maxima can be seen around the metal, with one pointing toward the center of the benzene ring. The maxima appear sharper in the theoretical map, in spite of the fact that it has been corrected for the effects of thermal motion.[7] The deformation density in an equivalent plane passing

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(1) Kok, R. A.; Hall, M. B. *J. Am. Chem. Soc.* **1985**, *107*, 2599–2604. The top part of Figure 1 is taken from Figure 3 of this paper, p 2602.

(2) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2516–2528.

(3) Troup, J. M.; Extine, M. W., unpublished results in ref 1.

(4) O'Connell, A. M.; Rae, A. I. M.; Maslen, E. N. *Acta Crystallogr.* **1966**, *21*, 208–219.

(5) Data were collected from a prismatic crystal, 0.24 × 0.20 × 0.33 mm, at 100 K on an Enraf–Nonius CAD-4 diffractometer using Mo Kα ($\lambda = 0.71069$ Å) X-radiation. The diffraction data were measured up to θ of 46° ($\psi = 0°$); in addition, reflections in the range $\theta < 20°$ were measured at $\psi = \pm 15°, \pm 30°, \pm 45°$, making a total of seven equivalents in this range. For $22° < \theta < 40°$ reflections were also collected at $\psi = 15°$. In total 16444 reflections were measured. Data were corrected for the effects of absorption (grid point 7 × 7 × 11) and averaged to give a total of 2590 unique reflections ($R_{av} = 0.012$), among which 2484 reflections were observed ($F_o > 4\sigma(F_o)$). Eighty strong reflections were measured without an attenuator at a lower X-ray source intensity and rescaled. Cell parameters were obtained by a least-squares fit to the θ values of 82 reflections. $a = 6.0328$ (6) Å, $b = 10.954$ (1) Å, $c = 6.5217$ (3) Å, $\beta = 100.675$ (4)° ($T = -173$ °C). $Z = 2$. Space group $P2_1/m$. The structure was refined by full-matrix least squares which included a secondary isotropic extinction correction ($g = 0.16$ (4) × 10^{-4}). The final agreement indices were $R(F) = 0.022$, $R_w(F) = 0.027$, where $w = 1/(\sigma^2(I) + (0.01 I_{net})^2)$. Positional and thermal parameters of non-hydrogen atoms used for calculation of the deformation density maps were obtained from high-order refinement by using data with $\sin\theta/\lambda > 0.75$ Å^{-1}; the hydrogen atom coordinates were determined by moving the hydrogen atoms from their positions obtained from full data refinement along the C–H vector until the C–H distance was 1.085 Å.[6] All the deformation density maps were calculated by using diffraction data with $\sin\theta/\lambda < 0.75$ Å^{-1}.

(6) Dunitz, J. D.; Seiler, P. *J. Am. Chem. Soc.* **1983**, *105*, 7056–7058.

0002-7863/87/1509-0587$01.50/0