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IR Polarization Directions in *s-trans*-1,3-Butadiene and the Average Topochemistry of the s-Cis to s-Trans Photoisomerization in Matrix Isolation

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Abstract: Vibrational transition moment directions of *s-trans*-1,3-butadiene were deduced from measurements of its IR linear dichroism on samples partially oriented (i) by photoselective photoisomerization of *s-cis*-1,3-butadiene isolated in inert-gas matrices with linearly polarized light, (ii) in stretched polyethylene, and (iii) in stretched poly(ethylene-d_4). The moment directions are in quite good agreement with those predicted by theory at the MP2/6-311G** level of approximation. With semiempirical methods and at very low levels of ab initio theory, the agreement is just as good for a few vibrations (C=C stretch, *as* CH_2 stretch) but poor for others. The average relative orientation of the C_1–C_4 axis of the s-cis starting material and the C_1–C_4 axis of the s-trans photoproduct in the matrix has been determined; the two directions nearly coincide. A general computational procedure for relating the orientation of reactant and product molecules for an arbitrary reaction path in the absence of net torque on the environment has been formulated. For two plausible mechanisms of s-cis to s-trans isomerization, it predicts the observed near coincidence of the C_1–C_4 directions. For another reaction path, it predicts a 30° angle between them. However, at present, it is unknown whether matrix photoisomerizations indeed proceed without exertion of a net torque on the environment.

It has been shown[1] that the IR linear dichroism (LD) of matrix-isolated *s-cis*-1,3-butadiene remaining after partial photoconversion to the s-trans isomer with linearly polarized 248-nm light is only compatible with all IR transition moments being directed along a set of orthogonal axes. Barring an unlikely coincidence, this requires an assignment of planar (C_{2v}) or nearly planar geometry to this minor conformer in rigid matrices, with a twist angle less than 15°. The measurement also yielded the symmetry assignments of the nine observed vibrations of the minor conformer as polarized along the x, y, or z symmetry-determined axes. A recent reinvestigation[2] reduced the error margin for the possible deviation from planarity to less than 10°, and extended the polarization assignments to the C–H stretching region.

Presently, the IR LD of the matrix-isolated C_{2h}-symmetry *s-trans*-1,3-butadiene product of the above photochemical transformation is analyzed and compared with the IR LD of this major 1,3-butadiene conformer in stretched polyethylene and stretched poly(ethylene-d_4). The combined experimental results provide information on (i) the IR transition moment directions in *s-trans*-1,3-butadiene, and (ii) the average spatial relation between the s-cis reactant and the s-trans product, i.e., the average topochemistry of the photochemical reaction. Either kind of information is normally accessible only in single-crystal environment.

The IR transition moment directions, permitted by symmetry to lie either perpendicular to the molecular plane or in any direction in the molecular plane of *s-trans*-1,3-butadiene, permit us to perform a sensitive test of the quality of ground-state molecular wave functions.

Experimental Part and Methods of Calculation

The details of the IR dichroism measurements in photooriented rare gas matrices[1,2] and in stretched polyethylene[3,4] were reported previously.

The calculations were performed using the Gaussian 86[5a] and CADPAC[5b] programs. The basis sets used in the ab initio calculations were STO-3G,[6] 6-31G,[7] 6-31G*,[8] 6-31G**,[8] 6-311G**,[9] and D95V** (Dunning–Hay 9s5p valence double zeta).[10] Transition moments were computed using the usual approximations of mechanical and electrical harmonicity. In the ab initio calculations, the transition moments were evaluated analytically.

Computations of the relative orientation of the reactant and product assumed no net torque on the environment and were performed by the method described in the Appendix, using MNDO-optimized geometries for reactant, product, and possible intermediates (bicyclobutane, 1,3-biradical).

Results and Discussion

Since the structure of this section is complicated, it will be useful to start by a general overview of its organization.

After a set of definitions of the molecular axes systems used in the following, we describe the results of measurement of IR dichroism on samples oriented by (i) photoselection in argon matrix, (ii) alignment in stretched polyethylene, and (iii) alignment in stretched poly(ethylene-d_4). We use the combined results of the three measurements to deduce quite accurately the moment directions of IR transitions relative to the molecular long axis, and then take recourse to theory to establish the direction of this axis in molecular framework, with an overall accuracy for absolute IR transition polarizations estimated at better than ±10°.

We then evaluate various levels of empirical, semiempirical, and ab initio theory with respect to their ability to predict the observed IR polarization directions, which clearly reveal interferences between simple local vibrational motions.

Remarkably, the matrix photoselection data establish the average relative orientation of the photoproduct, *s-trans*-1,3-butadiene, relative to the starting material, *s-cis*-1,3-butadiene. In the limiting case of zero torque by the matrix on the solute during photoisomerization, this carries information on the details of the mechanistic path, and we conclude by showing how this can be extracted if the limiting case indeed applies.

Molecular Axes. In the following, we shall need to refer to several sets of molecular x, y, z axes, one for *s-cis*-butadiene (unprimed) and three for *s-trans*-butadiene (primed, doubly primed, and triply primed). Although the three sets for the latter

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(1) Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 1056.

(2) Arnold, B. R.; Balaji, V.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 1808.

(3) Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 4268.

(4) Radziszewski, J. G.; Arrington, C. A.; Downing, J. W.; Balaji, V.; Murthy, G. S.; Michl, J. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *163*, 191.

(5) (a) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN 86* (COS version); Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984. (b) Amos, R. D.; Rice, J. E. *CADPAC: The Cambridge Analytic Derivatives Package*; Cambridge, 1987; Issue 4.0.

(6) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(7) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *54*, 2257.

(8) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

(9) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(10) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 3, p 1.

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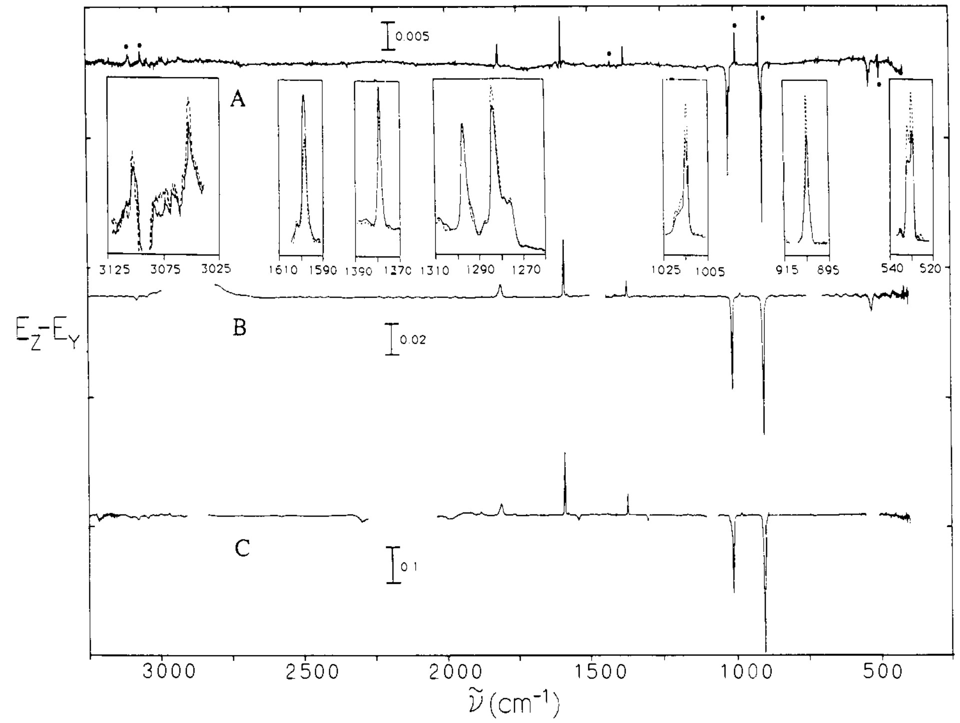

Figure 1. Linear dichroism of aligned *s-trans*-1,3-butadiene (10 K): (A) photooriented in argon matrix (peaks labeled with a dot belong to the s-cis conformer), (B) in stretched polyethylene, (C) in stretched poly(ethylene-d_4). E_Z and E_Y are absorbances measured with the electric field vector of the IR light oriented along laboratory axes Z and Y, respectively. In the argon matrix spectrum, absorbance recorded before irradiation has been subtracted in E_Z as well as E_Y. Representative examples of E_Z and E_Y peaks after such correction are shown for a few of the vibrations.

will later turn out to be identical within experimental error, this was not certain a priori.

In planar *s-cis*-1,3-butadiene (C_{2v}), z is used for the 2-fold symmetry axis, x for the out-of-plane axis, and y for the C_1–C_4 axis. Since the absorption at 248 nm is purely y-polarized,[1,2] y is the "depletion" axis in the photoselection process.

In *s-trans*-1,3-butadiene (C_{2h}), $z' \equiv z'' \equiv z'''$ is the out-of-plane axis of 2-fold symmetry. The y' axis is the "enrichment" axis in the argon-matrix photoselection experiment, i.e., that direction in the molecular framework which, on the average, is lined up the best with the electric vector direction Z of the light used to excite the starting s-cis isomer. Although, in principle, this could have been the out-of-plane direction, the results clearly show that it is not; hence y' lies in some initially unknown direction in the molecular plane. The y'' axis is the orientation axis of the s-trans isomer in stretched polyethylene, i.e., that direction in the molecular framework which, on the average, is lined up the best with the polymer stretching direction. The y''' axis is the orientation axis of the s-trans isomer in stretched poly(ethylene-d_4). All previous experience with the orientation of planar molecules in stretched polyethylene[3,11,12] suggests strongly that y'' and y''' will be collinear, or nearly so, and located in the molecular plane very close to the "long axis" of the molecule, i.e., close to the C_1–C_4 direction.

The x', x'', and x''' axes are defined by their orthogonality to the other axes.

Matrix Photoselection. In this subsection, we describe the IR linear dichroism of matrix-isolated *s-trans*-1,3-butadiene produced by irradiation of the s-cis isomer into a band polarized along its C_2–C_3 axis. The data are first analyzed with the assumption that all directions perpendicular to the absorbing transition moment are equivalent. Then, it is recognized that the relaxation of the hot reacting molecule may be anisotropic, even though a measurement of the rotation of the cold molecule in an annealed matrix is found to be quite isotropic. In this general case, we are left with a degree of freedom in the analysis of the data, and choose to remove it by demanding the best possible simultaneous agreement of all the experimental transition moment directions with those calculated at the MP2/6-311G** level of theory.

The initial sample of argon-matrix isolated randomly oriented 1,3-butadiene deposited through a hot oven contains significant IR bands of both the s-trans and s-cis conformers.[1,2,13-15] Enrichment in the s-cis form can also be accomplished by irradiation of the argon-matrix isolated s-trans form at 214 nm. However, 214-nm irradiation of *s-trans*-1,3-butadiene embedded in polyethylene does not cause this transformation.

Irradiation at 248 nm gradually converts the argon-matrix isolated s-cis form into the s-trans form, and measurements were performed at several stages of this process. In the following, we deal only with the IR intensities associated with the newly photoproduced s-trans conformer and always subtract out that part of the IR intensity that is due to the randomly oriented fraction of this material initially present in the matrix.

When the argon matrix irradiation is performed with linearly polarized 248-nm light whose electric vector lies along the laboratory Z direction, the photoproduced fraction of the s-trans conformer is uniaxially oriented with respect to Z and the matrix exhibits linear dichroism (Figure 1A). For each IR transition of the s-trans species, the photochemically induced absorbance increase E_Z measured with light polarized along the Z axis differs from the absorbance increase E_Y measured with light polarized along the Y axis. For each observable vibrational transition ν_i, the dichroic ratio $d_i = E_Z/E_Y$ can be measured for each of several degrees of sample conversion, and the orientation factors[11,12] K_i can be obtained from

$$K_i = \langle \cos^2 i \rangle = d_i/(d_i + 2) \qquad (1)$$

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(11) (a) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light, Solute Alignment by Photoselection, in Liquid Crystals, Polymers, and Membranes*; VCH: Deerfield, Beach, FL, 1986. (b) Thulstrup, E. W.; Michl, J. *Elementary Polarization Spectroscopy*; VCH: New York, 1989.

(12) Michl, J.; Thulstrup, E. W. *Acc. Chem. Res.* **1987**, *20*, 192. Thulstrup, E. W.; Michl, J. *Spectrochim. Acta* **1988**, *44A*, 767.

(13) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.

(14) Huber-Wälchli, P.; Günthard, Hs. H. *Spectrochim. Acta* **1981**, *37A*, 285.

(15) Huber-Wälchli, P. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 10. Furukawa, Y.; Takeuchi, H.; Harada, I.; Tasumi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 392.

Table I. Orientation Factors of *s-trans*-1,3-Butadiene Oriented by Photoselection on *s-cis*-1,3-Butadiene[a]

i	sym	ν_i (cm^{-1})	K_i	$\lvert\phi_i\rvert$[b]	$\lvert\phi_i^+\rvert$[c]	$\lvert\phi_i^-\rvert$[d]
1	a_g	3037	0.338 ± 0.005	55–60	54–58	57–63
2	a_g	3016	0.357 ± 0.005	46–51	46–50	47–52
3	a_g	2994	0.39 ± 0.010	29–38	31–39	25–37
6	a_g	1279	0.31 ± 0.010	67–90	63–75	72–90
7	a_g	1206	0.32 ± 0.010	61–74	59–69	65–90
10	a_u	1012	0.265 ± 0.005	90	90	90
11	a_u	904	0.273 ± 0.005	90	90	90
12	a_u	537	0.263 ± 0.005	90	90	90
17	b_u	3105	0.320 ± 0.005	64–70	61–66	68–78
18	b_u	3060	0.309 ± 0.005	71–80	66–72	79–90
19	b_u	2985	0.343 ± 0.010	52–61	51–59	53–65
20	b_u	1596	0.422 ± 0.005	9–18	17–23	0–10
21	b_u	1379	0.381 ± 0.005	36–40	37–41	34–39
22	b_u	1293	0.337 ± 0.005	55–60	54–58	57–63
23	b_u	984	0.417 ± 0.005	14–22	20–26	0–16

[a] Argon matrix, irradiation at 248 nm, interrupted at 23% conversion, when the orientation factors of the remaining *s-cis*-1,3-butadiene were $K_y = 0.29$ and $K_x = K_z = 0.355$. [b] $\lvert\phi_i\rvert$ is the absolute value of the angle between the ith transition moment and the z' axis (in degrees), obtained from eq 3 and $K_{x'} = 0.30$, $K_{y'} = 0.43$, $K_{z'} = 0.27$. [c] Absolute value of the angle between the ith transition moment and the z' axis (in degrees), obtained from eq 3 and $K_{x'} = 0.29$, $K_{y'} = 0.44$, and $K_{z'} = 0.27$. [d] Absolute value of the angle between the ith transition moment and the z' axis (in degrees), obtained from eq 3 and $K_{x'} = 0.31$, $K_{y'} = 0.42$, and $K_{z'} = 0.27$.

where i is the angle between the direction of the ith transition moment and Z, and the pointed brackets indicate ensemble averaging. The degree of conversion is determined from the isotropic absorbance $(E_Z + 2E_Y)/3$.

For all degrees of conversion, the degree of orientation of the remaining s-cis isomer is revealed by the orientation factors K_x, K_y, and K_z of its x, y, and z axes, respectively. It is lower than expected from theory[11a] for an optically thin sample. This is not surprising, considering that in our experiments the initial optical density at 248 nm was typically as high as 3 in order to provide sufficient absorbance for accurate measurements in the IR region. Also, some fraction of the excited s-cis molecules may possibly return to the s-cis ground state in an orientation different from the one they had before absorbing a photon, thus causing further deviations from the behavior expected theoretically for an optically thin sample.

As the *s-trans*-1,3-butadiene photoproduct has C_{2h} symmetry, one of its principal orientation axes, x', y', or z', must be perpendicular to the molecular plane while the other two lie in this plane.

The value of the orientation factor of the out-of-plane axis follows immediately from the measured dichroic ratios of the out-of-plane polarized[16,17] a_u vibrations at about 537 cm^{-1} (ν_{12}), 904 cm^{-1} (ν_{11}), and 1012 cm^{-1} (ν_{10}), using eq 1. All three ratios were always found to be equal, as expected for a C_{2h} molecule. The numerical value of this orientation factor gradually changes with the degree of photochemical conversion, but is always less than 1/3. For the enrichment axis, the factor would be larger than 1/3. We conclude that the enrichment axis y' is perpendicular to the out-of-plane direction and label the latter z'.

In order to characterize the orientation distribution of the s-trans photoproduct sufficiently for any one degree of photoconversion, we therefore need to determine only one unknown orientation factor, say $K_{y'}$, and one unknown direction in the molecular plane, say y'. The third orientation factor follows from the properties of direction cosines,

$$K_{x'} = 1 - K_{y'} - K_{z'} \qquad (2)$$

and the direction of the x' axis is orthogonal to y' and z'. The K_i values listed in Table I refer to 23% photoconversion, for which $K_{z'} = 0.27$. They define the experimental values but not the signs of the angles ϕ_i between the in-plane transition moment directions and the y' axis through eq 3[11,12,18] as a function of a single unknown parameter $K_{y'}$.

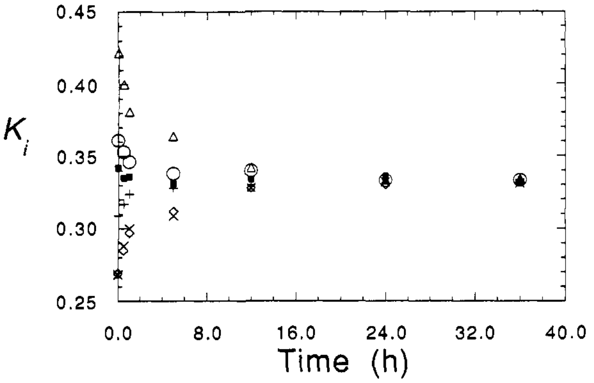

Figure 2. Orientation factors K_i of vibrations ν_i of *s-trans*-1,3-butadiene isolated in argon matrix at ~38 K as a function of time: i = 1 (■), 2 (○), 10 (◇), 11 (×), 18 (+), and 20 (△).

$$\tan^2 \phi_i = (K_{y'} - K_i)/(K_i - K_{x'}) \qquad (3)$$

In order to determine absolute IR polarization directions, the position of the y' axis in the molecular frame also needs to be determined. This shall be done by comparison with stretched sheet data and with calculations.

At first sight, the determination of $K_{y'}$ appears easy. In an average sense, the direction of the enrichment axis of a product of a photoselection process coincides with the direction of the depletion axis of the starting material in the system of axes defined for the reactant. Since the absorption of the reactant, *s-cis*-butadiene, is purely y-polarized at the 248-nm wavelength used,[1,2] y is its depletion axis, and the excitation process does not differentiate the x and z axes. Indeed, at all degrees of conversion, both are always oriented equally well in the remaining s-cis material ($K_x = K_z$).[1,2] In photoselection experiments on large and rigid molecules in highly viscous media, the absolute orientations of the y and y' axes in space are normally assumed to coincide for each reacting molecule (e.g., when the starting molecule and the product molecule do not differ in their shape but merely by their state of electronic excitation or by a proton shift).[11] Then, the photoselection process would not only fail to differentiate between the x and z axes of the remaining starting material, but also between the x' and z' axes of the product, and we would expect $K_{z'} = K_{x'} = (1 - K_{y'})/2$. Since $K_{z'}$ is known, this relation fixes the values of $K_{x'}$ and $K_{y'}$, and thus the absolute values of the angles ϕ_i.

However, the butadiene molecule is small and might undergo a more or less random rotational diffusion during and for a short time after the photochemical event, which generates well over 100 kcal/mol of local heat that needs to be dissipated. Such diffusion clearly is not extensive since this would destroy the net alignment of the photoproduct completely, but need not be absent altogether. As long as the randomizing rotation is isotropic, it will not perturb the relation $K_{z'} = K_{x'}$ and will merely bring both of these orientation factors, as well as $K_{y'}$, closer to the isotropic value 1/3 by reducing the degree of orientation.

We have investigated the isotropy of rotational diffusion of both the s-cis and s-trans isomers by measuring the dichroism of the aligned samples as a function of time at ~38 K and found no evidence for anisotropy (Figure 2). Of course, this result applies to vibrationally very cold molecules, and it is conceivable, if unlikely, that the rotation of highly vibrationally excited 1,3-butadiene is more strongly anisotropic. Still, the assumption $K_{z'} = K_{x'}$ appears sensible and was adopted in the pedagogical treatment given in ref 11b. However, it leads to a set of transition moment angles ϕ_i that all lie in the range ±(30–60°) and this looks

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(16) Panchenko, Yu. N. *Spectrochim. Acta* **1975**, *31A*, 1201.

(17) Cole, A. R. H.; Mohay, G. M.; Osborne, G. A. *Spectrochim. Acta* **1967**, *23A*, 909.

(18) Michl, J.; Thulstrup, E. W.; Eggers, J. H. *J. Phys. Chem.* **1970**, *74*, 3878.

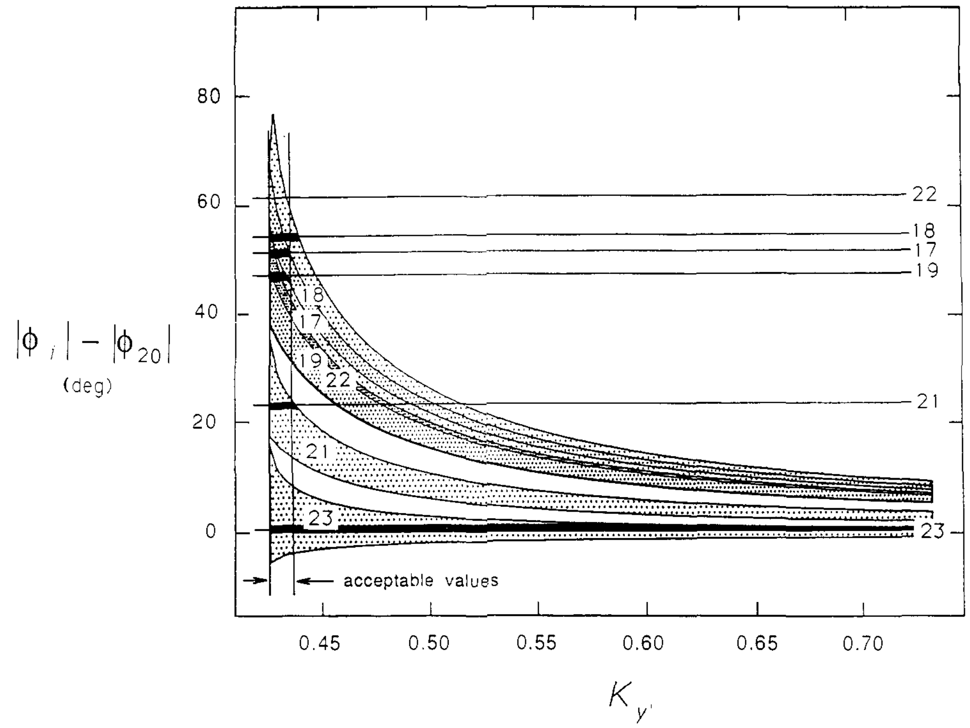

Figure 3. Differences $|\phi_i| - |\phi_{20}|$ of angles calculated from the K_i values measured in argon matrix (Table I), evaluated for all possible values of $K_{y'}$. Horizontal lines show the $|\phi_i| - |\phi_{20}|$ values computed at the MP2/6-311G** level.

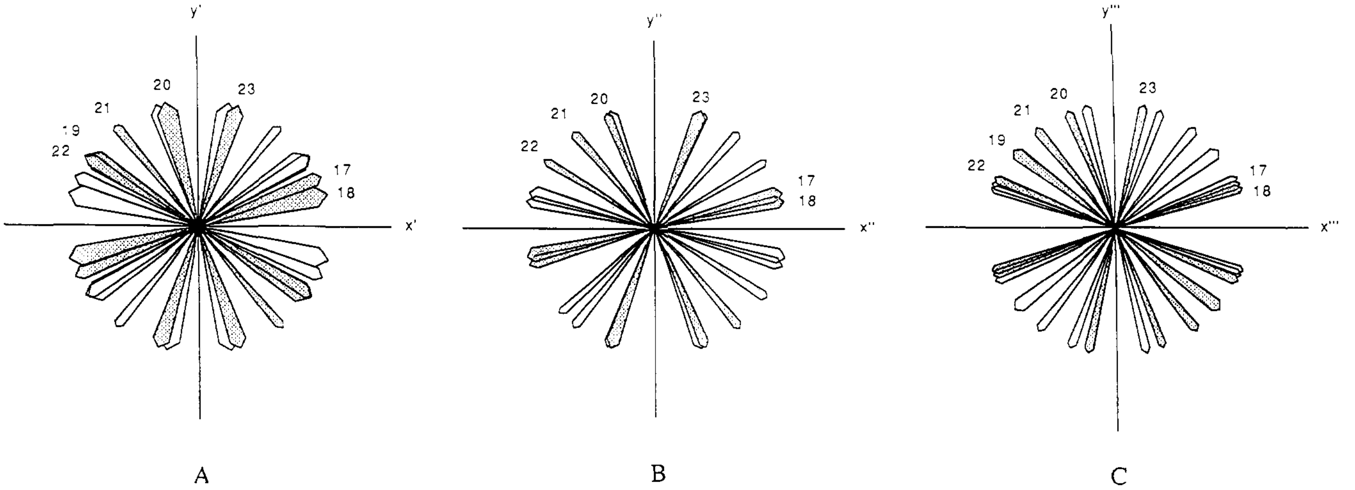

Figure 4. Transition moment directions for vibrations ν_i of *s-trans*-1,3-butadiene. For each *i*, two directions are compatible with the experimental data; the one that agrees better with the MP2/6-311G** calculation is shown in gray: (A) from argon matrix data only, relative to y', (B) from polyethylene data, relative to y'', (C) from poly(ethylene-d_4) data, relative to y'''.

suspicious. Therefore, we next reluctantly admit that we may be dealing with a general case of anisotropic rotation for which the condition $K_{z'} = K_{x'}$ cannot be imposed. It is then not possible to derive the value of the parameter $K_{y'}$ from the experimental data on hand. Instead, we are forced to let $K_{y'}$ range freely through all physically possible values. We shall fix this single degree of freedom by requiring the best possible simultaneous agreement of all the experimental transition moment directions with those calculated in an a priori fashion at the best level we were able to afford, MP2/6-311G**. Our results will then no longer be purely experimental, but we feel that this is the best way to proceed at present. If it becomes possible in the future to fix this one degree of freedom in a more satisfactory way, the transition moment directions can be reevaluated easily.

Figure 3 shows the differences $|\phi_i| - |\phi_{20}|$ calculated from the K_i values of Table I, obtained for 23% photoconversion, plotted against all possible assumed values of $K_{y'}$. The value $K_{z'}$ for this degree of photoconversion was 0.27, as dictated by the results for $\nu_{10} - \nu_{12}$ (Table I). The thickness in the bands shown in Figure 3 reflects the experimental uncertainty in the measured K_i values. The choice of ϕ_{20} as our reference angle was for convenience only, and any other vibration would have done equally well in principle. The advantage of this particular choice is that all the $|\phi_i| - |\phi_{20}|$ values are positive.

The $|\phi_i| - |\phi_{20}|$ values calculated at the MP2/6-311G** level intersect the experimental $|\phi_i| - |\phi_{20}|$ bands in the fat intervals show in the plot. The minimum of the least squares of the differences between the calculated and measured values of $|\phi_i| - |\phi_{20}|$ occurs at $K_{y'} = 0.43$, and a value of $K_{y'}$ near 0.43 will provide simultaneous agreement for all vibrations except ν_{22} (Figure 3, Table II). It is perhaps not a coincidence that ν_{22} is one of those vibrations whose calculated transition moment direction varies the most with the level of calculation. The value $K_{y'} = 0.43$ is also the least-squares minimum when using the angles $|\phi_i| - |\phi_{20}|$ provided by most of the other large basis set calculations. For 23% photoconversion, we therefore adopted $K_{z'} = 0.27 \pm 0.01$, $K_{y'} = 0.43 \pm 0.01$, and $K_{x'} = 0.30$ as the orientation factors for the principal axes in argon, and eq 3 yielded the absolute values

Table II. Comparison of Calculated and Experimental Transition Moment Directions Relative to ν_{20}

	$(\|\phi_i\| - \|\phi_{20}\|)$			$(\|\phi_i\| - \|\phi_{20}\|)$	
i	calc[a]	exp[b]	i	calc[a]	exp[b]
17	56	53 ± 7	21	26	24 ± 6
18	53	62 ± 9	22	63	44 ± 7
19	49	43 ± 9	23	1	4 ± 8

[a] MP2/6-311G** calculation. [b] From eq 3 using the experimental K_i values of Table I, $K_{x'} = 0.30$, and $K_{y'} = 0.43$ obtained by the least-squares minimization of the difference between the experimental and the calculated values of $|\phi_i| - |\phi_{20}|$.

of the angles ϕ_i between the *i*th vibrational transition moment direction in the s-trans product and the direction of the "enrichment" axis y' (Figure 4A, Table I). Since the direction of y' in the molecular framework is not known, the angles ϕ_i only contain information about the relative orientation of the IR transition moments in *s-trans*-1,3-butadiene. Because of the way in which ϕ_i enters eq 3, the sign of ϕ_i cannot be determined, and both choices, $\pm\phi_i$, are shown in Figure 4. For each *i*, the choice that agrees more closely with the result of the MP2/6-311G** calculation is shown in gray.

In summary, then, a single appropriate choice of the orientation factor $K_{y'}$, close to the value that corresponds to the intuitively expected relation $K_{z'} = K_{x'}$, brings the experimentally derived relative transition moment directions of six of the seven observed in-plane polarized vibrations, determined with errors less than ±10°, into agreement with MP2/6-311G** theory.

It will be noted that in addition to the results for vibrations of a_u and b_u symmetries, Table I also contains entries for seven gerade vibrations, IR-forbidden in an isolated molecule. Their intensity varies as a function of the matrix material but is sufficient for a determination of a polarization direction. Their appearance in the argon-matrix IR spectra has been noted previously[14,15] and must be due to matrix perturbations. Such matrix perturbation effects are relatively common, and we have also observed them in the IR spectrum of *s-cis*-1,3-butadiene.[1,2] These perturbations might be expected to affect polarization directions of weak ungerade vibrations as well. We have therefore used several different matrices in our work but have not noticed any systematic differences between them. This leads us to assume in the following that such matrix perturbations of the IR polarization directions for the allowed fundamental vibrations of *s-trans*-1,3-butadiene are smaller than our experimental uncertainties.

Linear Dichroism in Stretched Polyethylene. In order to anchor the transition moment directions to the molecular framework and to obtain results for additional vibrations, we have measured the linear dichroism of 1,3-butadiene in stretched polyethylene. In this uniaxial medium, planar molecules tend to orient so as to display the smallest possible cross section when viewed along the stretching axis *Z*, with their out-of-plane axis aligned the worst and their "long" in-plane axis aligned the best with *Z*.[3,11,12] The orientation factors of the molecular axes, needed for the evaluation of IR transition moment directions, are normally not easily determined for molecules of low symmetry. However, we shall find that in our case they can be obtained unequivocally from the requirement that the relative IR transition moment directions of *s-trans*-1,3-butadiene be the same in polyethylene and in argon matrix.

As expected, only the IR transitions of the major conformer, the s-trans species, were observed in the stretched sheet spectra. The observed orientation factors K_i^H for this partially aligned sample of *s-trans*-1,3-butadiene are listed in Table III. The out-of-plane polarized transitions share the value $K_{z''}^H = 0.23 \pm 0.01$, so that $K_{x''}^H + K_{y''}^H = 0.77 \pm 0.01$, where z'' is the out-of-plane axis and y'' is the in-plane orientation axis of *s-trans*-1,3-butadiene in stretched polyethylene. For in-plane polarized transitions we have $K_{y''}^H \geq K_i^H \geq K_{x''}^H$. Since $K_{x''}^H$ must be smaller than or equal to the smallest observed value of an orientation factor of an in-plane vibration (0.29 for ν_1, Table III), the smallest possible value of $K_{y''}^H$ is 0.48, in which case $K_{x''}^H = 0.29$. The largest possible value of $K_{y''}^H$ is 0.77, since $K_{x''}^H$ cannot be negative. The absolute values of the angle θ_i between the moment direction of the *i*th transition and the orientation axis y'' are again given by eq 3, with ϕ_i, $K_{y'}$, and $K_{x'}$ replaced by θ_i, $K_{y''}$, and $K_{x''}$, respectively. If the values of $K_{y''}^H$ and $K_{x''}^H$ could not be determined within much narrower error limits, the uncertainty of the resulting angles θ_i would be so large as to make them virtually useless, except for establishing the order in which they deviate from y'', dictated by the order of decreasing K_i^H values in Table III.

Table III. Orientation Factors of *s-trans*-1,3-Butadiene in Stretched Polyethylene (K_i^H) and Poly(ethylene-d_4) (K_i^D) and Transition Moment Directions Relative to z'' and z''' Axes

i	sym	ν_i^H (cm^{-1})	K_i^H	$\|\theta_i^H\|$[a]	ν_i^D (cm^{-1})	K_i^D	$\|\theta_i^D\|$[b]
1	a_g	3021	0.353 ± 0.005	52–55	3019	0.345 ± 0.005	55–58
2	a_g	2996	0.390 ± 0.02	38–48	2996	0.402 ± 0.005	39–42
3	a_g				2980		
4	a_g	1637	0.330 ± 0.01	58–64	1637	0.375 ± 0.005	46–49
5	a_g	1434	0.335 ± 0.005	58–61	1434	0.341 ± 0.005	56–59
6	a_g				1279	0.329 ± 0.005	59–62
7	a_g				1206	0.333 ± 0.005	58–61
10	a_u	1012	0.235 ± 0.005	90	1012	0.234 ± 0.005	90
11	a_u	904	0.238 ± 0.005	90	904	0.228 ± 0.005	90
12	a_u	537	0.232 ± 0.005	90			
17	b_u	3082	0.299 ± 0.005	70–75	3082	0.307 ± 0.005	67–71
18	b_u	3043	0.291 ± 0.005	74–80	3042	0.302 ± 0.005	69–73
19	b_u				2970	0.361 ± 0.005	50–53
20	b_u	1590	0.459 ± 0.005	1–24	1594	0.463 ± 0.005	19–23
21	b_u	1374	0.410 ± 0.005	37–40	1374	0.411 ± 0.005	36–39
22	b_u	1290	0.346 ± 0.005	55–58	1290	0.316 ± 0.005	64–67
23	b_u	984	0.464 ± 0.005	18–23	984	0.478 ± 0.005	10–17

[a] $|\theta_i^H|$ is the angle in degrees between the *i*th transition moment direction and the y'' axis, obtained by using eq 3 and $K_{y''}^H = 0.48 \pm 0.01$ and $K_{x''}^H = 0.29 \pm 0.01$ (see text). [b] $|\theta_i^D|$ is the angle in degrees between the *i*th transition moment direction and the y''' axis, obtained by using eq 3 and $K_{y'''}^D = 0.49 \pm 0.01$ and $K_{x'''}^D = 0.28 \pm 0.01$ (see text).

It is possible to narrow down the range of permissible values of $K_{y''}^H$, and therefore $K_{x''}^H$, that describe the stretched polymer sample, by demanding that the values of the six angles between the seven in-plane moment directions of the transitions $\nu_{17} - \nu_{23}$ be the same no matter in which of the two totally independent determinations they originate, matrix photoselection or alignment in a polymer. For convenience, we again choose the transition moment direction of ν_{20} as our reference. We only know the absolute values of the angles ϕ_i and θ_i, and therefore demand an equality, within experimental error, of the differences $|\phi_i| - |\phi_{20}|$ and $|\theta_i| - |\theta_{20}|$ for i = 17–19 and 21–23.

Figure 5 shows the differences $|\theta_i| - |\theta_{20}|$ calculated from the stretched polyethylene data plotted against all possible $K_{y''}^H$ values. The thickness of the strips corresponds to the uncertainties caused by the errors in the measured dichroic ratios. Also shown are horizontal strips indicating the $|\phi_i| - |\phi_{20}|$ values derived above from the matrix photoselection data, and their thickness again reflects the experimental error bars. The dark regions are defined by the intersections of the strips for $|\theta_i| - |\theta_{20}|$ and $|\phi_i| - |\phi_{20}|$. It is seen that all six equalities, for i = 17–19 and 21–23, can be satisfied simultaneously. This provides support for our assumption that the polarization directions of the intense fundamentals are essentially independent of the environment.

However, it is only possible to satisfy all equations at the same time in the narrow region of values $K_{y''}^H = 0.48 \pm 0.01$. This defines the orientation factors of *s-trans*-1,3-butadiene in stretched polyethylene with adequate accuracy. We adopt the values $K_{z''}^H = 0.23 \pm 0.01$, $K_{x''}^H = 0.29 \pm 0.01$, and $K_{y''}^H = 0.48 \pm 0.01$.

The use of eq 3 with ϕ_i, $K_{y'}$, and $K_{x'}$ replaced by θ_i^H, 0.48 ± 0.01, and 0.29 ± 0.01, respectively, now yields the complete set of angles $|\theta_i^H|$ listed in Table III and shown in Figure 4B. Again, both possible choices $\pm\theta_i^H$ are shown and the one that agrees better with the MP2/6-311G** calculation is displayed in gray.

We have now expanded our list of observed in-plane polarized vibrations to 10, and shown that the IR polarization directions derived from photoselection in argon matrix are perfectly compatible with the totally independent set of measurements in stretched polyethylene. As is clear from a comparison of parts A and B of Figure 4, in doing so, we have also significantly reduced

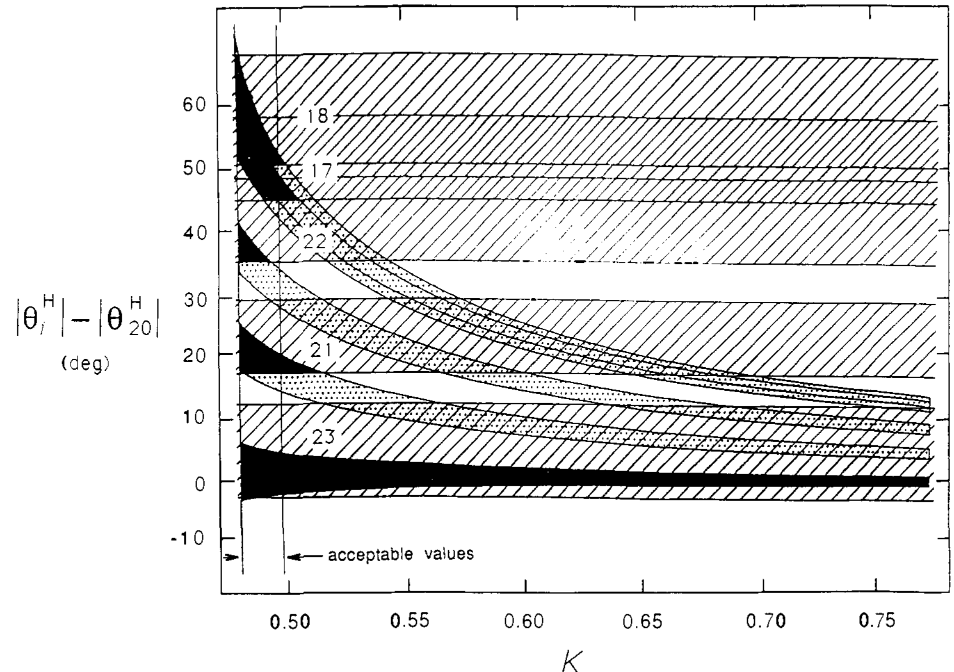

Figure 5. Differences of angles $|\theta_i^H| - |\theta_{20}^H|$ calculated from the K_i values measured in stretched polyethylene (Table III), evaluated for all possible values of $K_{y''}$. Horizontal strips represent the $|\phi_i| - |\phi_{20}|$ values from argon matrix measurements.

the error margins in the determined angles. Strictly speaking, these results are still all for relative polarizations and are not tied to the molecular framework, but all previous experience with the orientation of solutes in stretched polyethylene[11,12] suggests that y'' must lie within a few degrees of the "long" axis of the molecule, i.e., very close to the C_1–C_4 direction.

Linear Dichroism in Stretched Poly(ethylene-d_4). A third determination of the relative transition moment directions is available from measurements in stretched perdeuterated polyethylene. It provides yet another independent verification of the IR transition moment directions deduced so far, and further increases our confidence level that they are indeed correct.

Only a high-density polyethylene sample was available to us. This often orients solutes somewhat less well than low-density polyethylene, but in the present case the degrees of orientation were comparable in the two polymers (cf. the K_i^D values in Table III). The orientation factor common to the out-of-plane polarized a_u vibrations is $K_{z'''}^D = 0.23 \pm 0.01$. Proceeding exactly as above for ordinary polyethylene and comparing the results from poly(ethylene-d_4) with the argon matrix data, we derive the values $K_{x'''}^D = 0.280 \pm 0.015$ and $K_{y'''}^D = 0.490 \pm 0.015$. The use of eq 3 with ϕ_i, $K_{y'}$, and $K_{x'}$ replaced by θ_i^D, 0.490 ± 0.015, and 0.280 ± 0.015, respectively, now yields a third independent set of angles $|\theta_i^D|$ listed in Table III and shown in Figure 4C. Once again, both choices, $\pm\theta_i^D$, are shown and the one that agrees better with the ab initio calculation is colored gray.

The $|\theta_i^D|$ values obtained from the perdeuterated polymer sample agree with the $|\theta_i^H|$ values obtained from ordinary polyethylene and, not surprisingly, show that the molecular orientation axes of *s-trans*-1,3-butadiene in the two polymers coincide, $y'' \equiv y'''$.

Both sets of the $|\theta_i|$ values also agree with the $|\phi_i|$ values, demonstrating that the photoselection enrichment axis y' also happens to coincide with y'' and y'''. This is unfortunate, since it does not permit an experimental determination of the relative signs of the angles θ_i that define the transition moment directions.

IR Transition Moments. The final set of best experimental polarization directions $|\theta_i|$ relative to the $y' \equiv y'' \equiv y'''$ axis, which is assumed to lie in the C_1–C_4 direction, was obtained from the three combined independent measurements, and is shown in Table IV and Figure 6, with conservative error estimates, about ±5° for most transitions. This represents the accuracy of relative IR transition moment directions. Because of the uncertainty in the absolute location of the $y' \equiv y'' \equiv y'''$ axis in the molecular framework, we estimate the accuracy of the absolute IR polarization determination to be ±10°. Data of this type are available for remarkably few molecules of low symmetry, and it is hoped that the present results will be found useful for purposes such as

Table IV. Transition Moment Directions of *s-trans*-1,3-Butadiene[a]

i	sym	ν_i[b]	$\lvert\theta_i\rvert$
1	a_g	3021	56 ± 4
2	a_g	2996	45 ± 4
3	a_g	2980	30 ± 4
4	a_g	1637	48 ± 7
5	a_g	1434	58 ± 4
6	a_g	1279	72 ± 10
7	a_g	1206	64 ± 6
10	a_u	1012	90
11	a_u	904	90
12	a_u	537	90
17	b_u	3082	68 ± 5
18	b_u	3043	74 ± 5
19	b_u	2970	54 ± 5
20	b_u	1590	21 ± 5
21	b_u	1374	38 ± 3
22	b_u	1290	59 ± 6
23	b_u	984	18 ± 5

[a] Angles in degrees, obtained by averaging all three sets of data, $|\phi_i|$, $|\theta_i^H|$, and $|\theta_i^D|$, assuming $y' \equiv y'' \equiv y'''$. Error bars are estimated.
[b] Values for polyethylene or perdeuterated polyethylene (cm^{-1}).

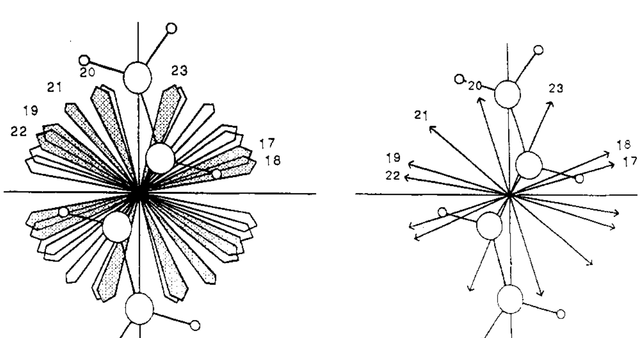

Figure 6. The best experimental (left, combined from Figure 4A,B,C, with $y' \equiv y'' \equiv y'''$) and calculated (right) transition moment directions, in molecular framework. See text.

testing computed wave functions.

It is important to recognize the limitations of what has been accomplished, however. In addition to being partly based on comparison with theory, the results suffer from two shortcomings. First, we do not know the signs of the angles θ_i. Second, the choices made in gray in Figure 6 are merely those that agree better with theory, and our assertion that we know the location of the $y' \equiv y'' \equiv y'''$ axis in the molecular framework to be very close to the C_1–C_4 direction represents an empirical extrapolation from past data on high-symmetry molecules and cannot be considered an absolute certainty. Indeed, no information on either point can be derived rigorously from our experimental data. Thus, at this time, further progress requires additional theoretical insight.

In the following, we compare the results with those obtained at the ab initio Hartree–Fock and MP2 levels of calculation for a series of basis sets, and with qualitative expectations based on the assumption of simple coupling of local motions in the molecule.

Comparison with Calculations. Although one general degree of freedom in the evaluation of the experimental results, as well as a sign ambiguity for each transition moment, was removed by comparison with quantum chemical calculations, the large number of transition moment directions that have been determined still justify the claim that a meaningful test of theory is possible. We have used a series of semiempirical and ab initio methods of calculation to obtain predictions of transition moment directions for the in-plane polarized fundamental vibrations in *s-trans*-1,3-butadiene (Table V). Convergence upon basis set increase is slow. This is not surprising, considering how hard the accurate calculation of IR intensities is.[19]

At the Hartree–Fock (HF) level, at least a 6-31G* basis set appears to be absolutely necessary and changes in direction by as much as 8° occur even upon going from 6-31G** to 6-311G**. It is therefore not clear that even our best calculations are closer to the Hartree–Fock limit than about ± 10°. Moreover, the introduction of correlation clearly has a significant effect on some of the transition moment directions, in particular, ν_{18} and ν_{19}. The calculated normal modes for these contain a mix of CH stretching and *sym* CH_2 stretching local motions. The differences in the HF and MP2 results are due to changes in the sign and magnitude of the interaction element. A similar problem seems to occur with ν_{22} and ν_{23}. At the MP2 level, the largest basis set we were able to use is still too small to ensure that the directions of all the transition moments have converged, although some apparently have, as the values computed with the best two basis sets agree within a few degrees. The best HF and MP2 results, obtained with the 6-311G** and D95V** basis sets, agree with the experimental values within about 10–20°, permitting a quite clear choice between the two presently experimentally indistinguishable signs of θ_i, and supporting our claim that the orientation axis is directed along the C_1–C_4 line (Figure 6). For each method of calculation, the best agreement with experiment is obtained for a slightly different assumed direction of the orientation axis. However, for all the highest level calculations, the optimized direction of the orientation axis is within 10° of the C_1–C_4 direction. In this sense, the calculations certainly support the standard notions concerning the location of the orientation axis for samples aligned in stretched polyethylene. The MP2 results are not significantly better than the HF results when it comes to agreement with experiment.

Some of the discrepancy between the calculated and the experimental values are undoubtedly due to experimental uncertainties in the measurement and to matrix effects. However, the slow convergence in the computed values suggests strongly that most of it is due to the deficiencies in the computation.

The possible problems are the accuracy of the derivatives of the dipole moments, of the force field, and of the normal modes; these could be addressed in a straightforward fashion by improvements in the basis set and in the treatment of electron

Table V. IR Transition Moment Directions of In-Plane (b_u) Vibrations of *s-trans*-1,3-Butadiene: Experiment and Calculation[a]

							HF						MP2			
i	ν_i^b	vibration	|exp|	MINDO/3	MNDO	AM1	STO-3G	6-31G	6-31G*	6-31G**	6-311G**	D95V**	6-31G	6-31G*	6-311G**	D95V**
17	3082	*as* CH_2 stretch	68 ± 5	−65	−54	83	−6	−66	−68	−68	−69	−70	−66	−69	−70	−72
18	3043	CH stretch	74 ± 5	−84	11	29	3	−47	−64	−66	−74	−72	81	84	−67	−65
19	2970	*sym* CH_2 stretch	54 ± 5	54	5	11	9	62	49	49	45	42	4	−22	63	72
20	1590	C═C stretch	21 ± 5	−76	16	29	22	13	11	11	11	10	16	16	14	16
21	1374	CH_2 scissors	38 ± 3	20	15	25	69	40	52	51	43	51	45	40	40	48
22	1290	"CH bend"	59 ± 6	11	17	36	3	47	39	41	46	48	70	73	77	80
23	984	"CH_2 rock"	18 ± 5	−83	−77	−24	−10	−19	−6	−3	−5	−14	−28	−23	−15	−23

[a] Angles in degrees. Calculated angles measured from C_1–C_4 axis away from C_2. Experimental angles measured from the $y'(\equiv y'' \equiv y''')$ axis. [b] Values for polyethylene or perdeuterated polyethylene (cm^{-1}).

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(19) E.g.: Yamaguchi, Y.; Frisch, M.; Graw, J.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262. Ahern, A. M.; Garrell, R. L.; Jordan, K. D. *J. Phys. Chem.* **1988**, *92*, 6228.

correlation when more computing power becomes available. More fundamental difficulties may lie in the assumptions of mechanical and electrical harmonicity. The neglect of Fermi resonances may be particularly serious. Possibly, even the Born–Oppenheimer approximation itself contributes to the disagreements.

Clearly, comparison of calculated IR transition moment directions with those determined experimentally offers an exquisitely sensitive means of testing the computed wave functions.

Comparison with Qualitative Expectations. A comparison with simple-minded expectations is instructive. In the absence of any mixing of nondegenerate individual local bond-stretching and bond-bending modes, the transition moment for a bond-stretching vibration can be expected to be directed along the bond, and that for an in-plane bond-bending vibration perpendicular to the bond. Vector addition yields the transition moments for vibrations involving several equivalent bonds, assuming equal weights for each of a group of degenerate local motions. This "group-vibration" description is only approximate since nondegenerate local motions surely also must mutually couple at least to some degree.

Using this naive concept, the polarization directions relative to the C_1–C_4 axis for ν_{19}, ν_{20}, and ν_{21} should all be equal to ~20°, for ν_{17} and ν_{23} to −70°, for ν_{18} to about 90°, and for ν_{22} to about 0°. All of these expectations are actually fulfilled within a 20–30° margin of error, except for two. These are the ν_{22} vibration at 1293 cm^{-1} (CH bend) and the ν_{23} vibration at 984 cm^{-1} (CH_2 rock). Inspection of the computed normal modes indicates that the CH_2 rocking and the CH bending motions are so strongly mixed that the labels cannot be meaningfully distinguished. It is then not surprising that this approach fails to predict the two transition moment directions correctly. Conversely, the measured IR transition moment directions provide direct experimental evidence that the ν_{22} and ν_{23} modes of vibration of *s-trans*-1,3-butadiene are due to strongly mixed local motions (vibrations ν_{18} and ν_{19} seem to represent a less severe case of this type of behavior).

This result represents bad news for the hopes that one shall be able to use the naive way of deriving IR transition moment directions for the anchoring of relative experimental IR polarization directions to molecular framework by means of IR LD measurements, an otherwise very attractive procedure.[20] On the bright side, this result demonstrates that measurements of IR polarization directions offer a very sensitive means of detecting interferences between local vibrational motions.

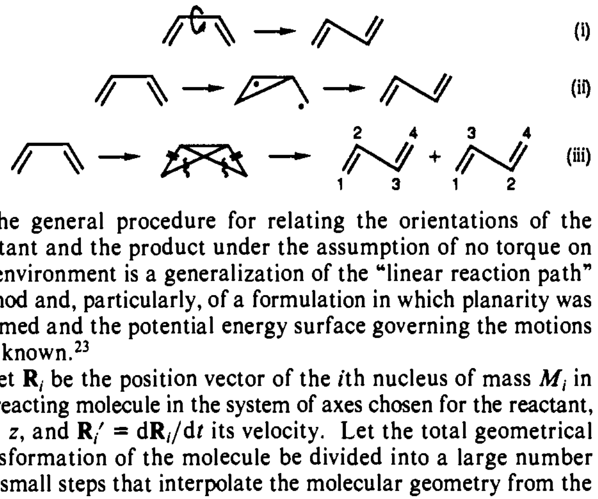
Topochemistry of the Photoisomerization. In spite of the partial rotational randomization of the orientation of the *trans*-1,3-butadiene photoproduct in argon matrix, the photoselection experiment has allowed us to establish the direction of the enrichment axis y' in the product as lying very close to the C_1–C_4 direction. This information provides a partial definition of the topochemistry of the reaction: on the average, the y (C_1–C_4) axis of the *s-cis*-1,3-butadiene reactant coincides with the C_1–C_4 axis of the *s-trans*-1,3-butadiene photoproduct. No information is available on the relative orientations of the x and x' or z and z' axes.

We are not aware of other examples of matrix photochemical reactions in which the average relative orientation of the starting material and the photoproduct has been established, but it appears likely that it will be possible to accumulate such information for additional reactions in the future. There is considerable interest in establishing just how much motional freedom reacting molecules have in rare gas matrices and in solids generally, so that a better understanding can be developed as to which of the photochemical processes known from fluid solution can be successfully performed in solid media. An example of an environmental effect of this kind was provided earlier in this study: in argon matrix, 214-nm irradiation converts *s-trans*-1,3-butadiene into the cis isomer, but in polyethylene, it does not.

If all molecules followed the same isomerization path in the nuclear configuration space, and if they exerted no torque on their environment, knowledge of the reaction path would be sufficient to establish the relative orientation of the C_1–C_4 axes of the reactant and of the product exactly. If two or more paths to the product existed, weighted averaging would be necessary. If the concurrent or subsequent partial rotational diffusion is random in the sense of tilting the y' axis with equal probability to either side in any plane in which the axis is contained, the average position of this axis will coincide with its position in the absence of such randomization.

Assuming that such is the case, we shall now demonstrate that the observed orientation of the y' direction agrees well with that expected for two of three hypothetical but reasonable mechanisms for the cis to trans photoisomerization if the reacting molecule does not exert any net torque on its environment. At present we do not know whether the assumption of zero torque is reasonable, so that this result does not permit us to exclude any of the three mechanistic possibilities considered. However, the procedure does suggest interesting possibilities for future mechanistic investigation of photoprocesses in solids.

The first mechanism to be considered, (i), is a simple internal rotation of the cis isomer about the C_2–C_3 bond, as would be expected for a hot ground-state process. The second, (ii), follows a lower symmetry path: disrotatory or conrotatory closure of a three-membered ring by C_1–C_3 bond formation in the cis isomer to yield a 1,3-biradical, followed by a disrotatory or conrotatory opening of the ring by C_1–C_3 bond breaking to yield *s-trans*-1,3-butadiene. Because hydrogen atoms are so light, the resulting product orientations are nearly identical for disrotatory and conrotatory ring closures and openings. The third mechanism to be considered, (iii), is a concerted two-ring closure of *s-cis*-1,3-butadiene to bicyclo[1.1.0]butane, followed by breaking the new C_1–C_3 and C_2–C_4 bonds or the old C_1–C_2 and C_3–C_4 bonds with equal probability to yield *trans*-1,3-butadiene. Bicyclo[1.1.0]butane is a known photochemical product from 1,3-butadiene[21] but is generally believed to originate from excitation of the s-trans isomer. However, since 1,3-cyclopentadiene, which is constrained to the s-cis diene geometry, photoisomerizes to tricyclopentane, either directly or via bicyclo[2.1.0]pent-2-ene,[22] an intermediacy of bicyclo[1.1.0]butane in the excited-state cis to trans isomerization of 1,3-butadiene is conceivable.



The general procedure for relating the orientations of the reactant and the product under the assumption of no torque on the environment is a generalization of the "linear reaction path" method and, particularly, of a formulation in which planarity was assumed and the potential energy surface governing the motions was known.[23]

Let $\mathbf{R}_i$ be the position vector of the ith nucleus of mass M_i in the reacting molecule in the system of axes chosen for the reactant, x, y, z, and $\mathbf{R}_i' = \mathrm{d}\mathbf{R}_i/\mathrm{d}t$ its velocity. Let the total geometrical transformation of the molecule be divided into a large number n of small steps that interpolate the molecular geometry from the initial to the final, and each of which occurs in unit time. They are chosen so as to leave the center of mass in place. The angular momentum generated by the motions of the individual atoms in going from the jth geometry, characterized by $\{\mathbf{R}_i(j)\}$, to the $(j + 1)$st geometry, characterized by $\{\mathbf{R}_i(j + 1)\}$, will be cancelled by an overall rotation of the molecule:

$$\sum_i M_i \mathbf{R}_i \times \mathbf{R}_i' = 0 \qquad (4)$$

For sufficiently small interpolation steps (large n), we can approximate $\mathbf{R}_i'$:

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(20) E.g.: Matsuoka, Y.; Nordén, B. *J. Phys. Chem.* **1982**, *86*, 1378.

(21) Srinivasan, R. *Adv. Photochem.* **1966**, *4*, 113.

(22) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 4851.

(23) Miller, W. H.; Ruf, B. A.; Chang, Y.-T. *J. Chem. Phys.* **1988**, *89*, 6298.

$$\mathbf{R}_i'(j) = \mathbf{R}_i(j+1) - \mathbf{R}_i(j) \qquad (5)$$

Since $\mathbf{R}_i(j) \times \mathbf{R}_i(j) = 0$, the condition on the adjacent interpolated geometries becomes

$$\sum_{i=1} M_i\mathbf{R}_i(j+1) \times \mathbf{R}_i(j) = 0 \qquad (6)$$

In order to satisfy this vector equation, a rotation by Euler angles α_j, β_j, and γ_j needs to be applied to an initial guess $\{\mathbf{R}_i^0(j+1)\}$ for $\{\mathbf{R}_i(j+1)\}$, which is typically generated by some scheme that defines the reaction path in terms of internal coordinates without regard to angular momentum. The three unknowns are determined from the vector equation (6) using the iterative multidimensional Newton–Raphson method (Appendix). The procedure is repeated from $j = 1$ to $j = n$ and yields the desired product geometry $\mathbf{R}_i(n)$ in the initial set of axes x, y, z. The whole process is repeated several times for increasing values of n until the results no longer change within the desired accuracy. In order to obtain an accuracy of 0.001 in cosine of the angle that the new position of the C_1–C_4 direction makes with the old one, this typically requires values of n equal to several hundred.

The scheme adopted to generate the initial guesses $\{\mathbf{R}_i^0\}$ relied on a specification of the molecular geometry in terms of bond lengths, valence angles, and dihedral angles. The reaction path is defined by specifying an initial, one or more intermediates, and a final geometry. Smooth connection from the reactant to the product is secured by interpolation of each of the internal coordinates. The procedure chosen allowed us to retard or advance the change in each internal coordinate with respect to the changes in the others. If f is the fraction of the reaction path covered, then for the ith internal coordinate $q_i(f)$ its fractional change $t_i(f)$ is given by

$$t_i(f) = fD_i^2/[(2D_i - 1)f + (D_i - 1)^2] \qquad (7)$$

so that

$$q_i(f) = q_i(0) + t_i(f)[q_i(1) - q_i(0)] \qquad (8)$$

where D_i is a parameter controlling the relative rate of change of the ith internal coordinate. For $D = 0.5$ the interpolation is linear, while for $D < 0.5$ most of the change is delayed until late in the reaction path, and for $D > 0.5$ most of the change occurs early.

We have written a computer program for the calculation of the product orientation given a reaction path, as defined by the initial, intermediate, and final geometries and the set of parameters D_i, and obtained the results for a fair number of paths. They are insensitive to details of the reaction paths, in particular, those involving light atoms, such as pyramidalization of CH_2 groups and their conrotatory versus disrotatory motions. They are influenced very strongly by those features of the reaction paths that involve noncancelling motions of carbon atoms.

Typical examples of the geometrical relation of the starting s-cis molecule to the s-trans product for the three paths (all $D = 0.5$) are shown in Figure 7. In each case, the view is along the 2-fold symmetry axis, with the C_1 and C_4 atoms of the s-cis isomer closer to the reader than its C_2 and C_3 atoms. Only one of the two possible product orientations is shown in each case; the other is obtained by mirror reflection in the plane of the reactant. Disrotatory and conrotatory motions gave results that are indistinguishable in the drawings shown.

The results for the first two of the three mechanistic paths considered for the *s-cis-* to *s-trans-*1,3-butadiene isomerization are similar. (i) Rotation around the C_2–C_3 bond, whether rigid or accompanied by minor distortions of the two vinyl groups at various stages of the reaction, yields orientations in which the original direction of the y (C_1–C_4) axis of the starting material, identical in space with the direction of the y' axis of the product, forms a 5 – 10° angle with the C_1–C_4 direction in the s-trans product, cutting through both the C_1–C_2 and C_3–C_4 bonds (Figure 7A). For mechanism ii, proceeding via a 1,3-biradical, the direction of the y' axis in the photoproduct again forms an angle of about 10° with its C_1–C_4 direction, inclined so as to cut the C_1–C_2 and C_3–C_4 bonds (Figure 7B). For path iii that proceeds via bicyclo[1.1.0]butane, half of the product molecules end up with the y' axis at an angle of ~20° from the C_1–C_4 direction, nearly parallel to the C_2–C_3 bond (Figure 7C). These are the molecules in which the original connectivity of the carbon chain is restored in the product. For the other half, the original y axis is located at a ~40° angle to the C_1–C_4 direction, inclined in the opposite direction, nearly parallel to the C_1–C_2 and C_3–C_4 bonds (Figure 7D). Since there is no correlation between the orientations of the individual molecules, such a composite assembly will behave as if the average direction of the y' axis in the photoproduct were located at ~30° to the C_1–C_4 axis.

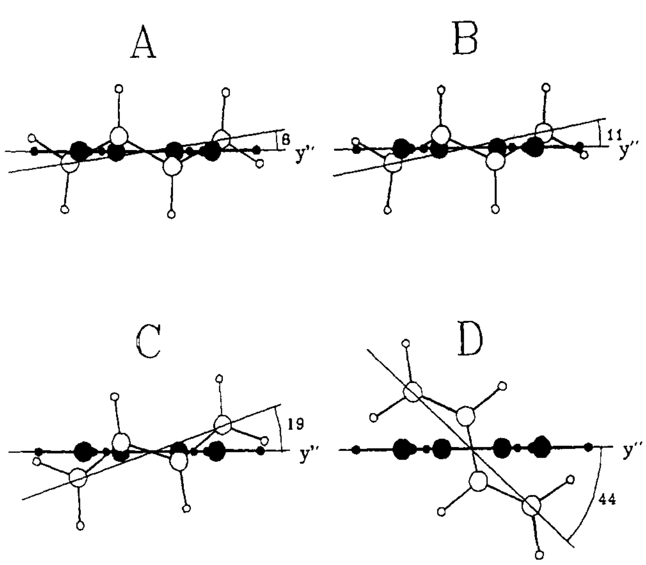

Figure 7. Computed spatial relation of an *s-cis*-1,3-butadiene reactant (black) and *s-trans*-1,3-butadiene product (white) for three reaction paths: (A) rotation about the C_2–C_3 bond, mechanism i; (B) closure to a 1,3-biradical followed by ring opening, mechanism ii; (C and D) closure to bicyclo[1.1.0]butane followed by connectivity-preserving and connectivity-reversing opening of both rings, respectively, mechanism iii. Zero torque on the environment is assumed.

The observed topochemistry, with y' along the C_1–C_4 axis, agrees with the expectation based on mechanisms i and ii, but not iii. Unfortunately, at this time we cannot be sure that the assumption of zero torque on the argon matrix environment is at least approximately correct, so that mechanism iii cannot be excluded. The situation may change in the future as additional photoprocesses are studied.

Mechanism iii could be eliminated by the more classical technique of isotopic labeling. Such a mechanistic investigation, however, lies beyond the scope of the present study, whose purpose has been to (i) determine the IR polarization directions in *s-trans*-1,3-butadiene, (ii) evaluate the suitability of various computational procedures for the calculation of these directions, (iii) demonstrate the feasibility of a topochemical investigation on a matrix-isolated species, and (iv) develop a general predictive procedure for topochemical behavior in the absence of torque on the environment.

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Appendix

In eq 6, we write the atomic position vectors $\mathbf{R}_i(j+1)$ as $\mathbf{R}_i^0(j+1)$ rotated by the Euler angles α_j, β_j, γ_j that are to be determined, and arrive at three equations, one for each Cartesian component of the angular momentum. These are of the form $F_n(\alpha,\beta,\gamma) = \Sigma_i c_{ni} f_{ni}(\alpha,\beta,\gamma) = 0$, $n = 1$–3. Here, c_{ni} are constants involving sums of products of the atomic coordinates in $\mathbf{R}_i^0(j+1)$ and $\mathbf{R}_i(j)$, and the functions $f_{ni}(\alpha,\beta,\gamma)$ are sums of products of sines and cosines of the unknown Euler angles. Adding the three identities,

J. Am. Chem. Soc. 1991, 113, 2919–2922

$$F_4(\alpha,\beta,\gamma) = \cos^2 \alpha + \sin^2 \alpha = 1$$

$$F_5(\alpha,\beta,\gamma) = \cos^2 \beta + \sin^2 \beta = 1$$

$$F_6(\alpha,\beta,\gamma) = \cos^2 \gamma + \sin^2 \gamma = 1$$

we obtain a system of six simultaneous equations in six unknowns that can be treated as independent and are collected in a vector $\mathbf{q} \equiv \{q_m\} \equiv \{\cos \alpha, \sin \alpha, \cos \beta, \sin \beta, \cos \gamma, \sin \gamma\}$:

$$F_n(\mathbf{q}) = H_n, \ n = 1\text{–}6$$

This equation set is solved iteratively. First, we choose an initial guess $\mathbf{q}^{(0)}$ and evaluate $h_n = F_n(\mathbf{q}^{(0)})$. From the partial derivatives of the functions of F_n with respect to the unknowns collected in $\mathbf{q}$, we have

$$\Delta F_n = \sum_m \Delta q_m (\partial F_n / \partial q_m)$$

as the linear approximation to the changes in the values of F_n that will be caused by a change $\Delta\mathbf{q}$ in the unknowns. To reach the solution, we would require $\Delta F_n = H_n - h_n$, $n = 1\text{–}6$. These six linear equations are solved for the Δq_m's. Since the functions F_n are not linear in q_m, it is necessary to take $\mathbf{q}^{(1)} = \mathbf{q}^{(0)} + \Delta\mathbf{q}$ and iterate. In practice, damping is usually required so that we actually set $\Delta F_n = (H_n - h_n)t$ for a suitably chosen $0 < t \ll 1$. Note that if the summation over m contained only one term, $m = 1$, and if there were only one function F_n, $n = 1$, then this iterative procedure would be exactly the Newton–Raphson method.

Registry No. *s-trans*-1,3-Butadiene, 106-99-0.

Infrared Spectroscopy at High Pressure. Interaction of N_2 with Rh/Al_2O_3 at Ambient Temperature

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Abstract: The design and construction of a new high-pressure infrared-cell reactor capable of variable-temperature operation which should be useful in the study of a variety of chemical reactions has been described. The cell reactor has been employed in this work to investigate the interaction of N_2 with Rh/Al_2O_3 catalyst films in the pressure regime 1×10^{-6} to 9000 Torr at 298 K. The results obtained were in good accord with those obtained by Wang and Yates for similar catalysts at low temperatures and pressures. Infrared bands for chemisorbed and physisorbed N_2 species have been detected and tentatively assigned.

I. Introduction

For the past decade work in these laboratories has focused on the use of transmission infrared spectroscopy to study the interaction of small molecules with supported transition-metal films, such as $CO/Rh/X$ ($X = Al_2O_3$, SiO_2, and TiO_2).[1] In particular studies of "simple" reactions such as the hydrogenation of CO[2] and CO_2[3] or the CO/NH_3 system[4] have provided intriguing information concerning the structures of intermediate species adsorbed on the supported catalyst films. Most of the prior work pertained to the reactions at sub-atmospheric pressure conditions, typically less than 100 Torr.[1-4] However, recent work here concerning the reaction of CO and CO_2 with H_2 over Pd/La_2O_3 films at high pressure (8000 Torr) to produce selectively methanol has led us to the conclusion that Fourier transform infrared spectroscopy can be employed to obtain useful information about reactions normally performed at several atmospheres of pressure.[5]

This paper will discuss the performance of a newly designed high-pressure infrared-cell reactor. The initial results obtained with the reactor, which will be addressed here, concerned the reaction of N_2 with Rh/Al_2O_3 films at 298 K as a function of pressure. While N_2 will interact with supported Rh catalysts at ambient temperatures or above if the support is TiO_2 or SiO_2 or if potassium promotion of Rh/Al_2O_3 is employed,[6-11] prior work on the unpromoted $N_2/Rh/Al_2O_3$ system has been confined to low-temperature studies because of the very weak interaction at ambient temperatures.[12] Indeed, the elegant investigation of Wang and Yates has demonstrated the considerable versatility of low-temperature infrared spectroscopy for studying the weak interaction of N_2 with Rh/Al_2O_3.[12] This paper will discuss the similarities and differences between the low-temperature, low-pressure work[12] and the current ambient-temperature, high-pressure studies.

II. Experimental Section

Schematic diagrams of the new high-pressure infrared-cell reactor used in this study are shown in Figures 1 and 2. The reactor was fabricated from three 4.62-in. stainless steel conflat flanges which were bolted together. The outer two flanges each contained 13-mm CaF_2 infrared windows held in place by 0.375-in. ultra-torr adaptor fittings. This arrangement allowed a base vacuum in the cell of ca. 1×10^{-8} Torr, as well as operating pressures of at least 13 atm. Both outer window assemblies could be cooled by flowing water. One of the outer flanges also contained ports for attachment to the vacuum and high-pressure manifolds and for gas chromatographic analysis. The middle flange

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(1) For a few examples see: Yang, A. C.; Garland, C. W. *J. Phys. Chem.* **1957**, *61*, 1504. Thornton, E. W.; Knozinger, H.; Tesche, B.; Rafalko, J. J.; Gates, B. C. *J. Catal.* **1980**, *62*, 117. Cavanagh, R. R.; Yates, J. T. *J. Chem. Phys.* **1981**, *74*, 4150. Rice, C. A.; Worley, S. D.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. *J. Chem. Phys.* **1981**, *74*, 6487. Worley, S. D.; Rice, C. A.; Mattson, G. A.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. *J. Chem. Phys.* **1982**, *76*, 20. Worley, S. D.; Rice, C. A.; Mattson, G. A.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. *J. Phys. Chem.* **1982**, *86*, 2714. McKee, M. L.; Worley, S. D. *J. Phys. Chem.* **1988**, *92*, 3699 and the numerous references quoted therein.

(2) Worley, S. D.; Mattson, G. A.; Caudill, R. *J. Phys. Chem.* **1983**, *87*, 1671.

(3) Henderson, M. A.; Worley, S. D. *Surf. Sci.* **1985**, *149*, L1. Henderson, M. A.; Worley, S. D. *J. Phys. Chem.* **1985**, *89*, 392. Henderson, M. A.; Worley, S. D. *J. Phys. Chem.* **1985**, *89*, 1417. McKee, M. L.; Dai, C. H.; Worley, S. D. *J. Phys. Chem.* **1988**, *92*, 1056.

(4) Paul, D. K.; McKee, M. L.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *J. Phys. Chem.* **1989**, *93*, 4598. Paul, D. K.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *J. Catal.* **1989**, *120*, 272; *Surf. Sci.* **1989**, *223*, 509; *Chem. Phys. Lett.* **1989**, *160*, 559.

(5) Dai, C. H.; Burkett, H. D.; Worley, S. D. *Chem. Phys. Lett.* **1990**, *173*, 430.

(6) Oh-Kita, M.; Aika, K. I.; Urabe, K.; Azaki, A. *J. Chem. Soc., Chem. Commun.* **1975**, 147.

(7) Oh-Kita, M.; Aika, K. I.; Urabe, K.; Ozaki, A. *J. Catal.* **1976**, *44*, 460.

(8) Resasco, D.; Haller, G. L. *J. Chem. Soc., Chem. Commun.* **1980**, 1150.

(9) Burch, R.; Flambard, A. R. *J. Chem. Soc., Chem. Commun.* **1981**, 965.

(10) Vishwanathan, V. *J. Chem. Soc., Chem. Commun.* **1989**, 848.

(11) Borod'ko, Yu. G.; Lyutov, V. S. *Kinet. Katal.* **1971**, *12*, 238.

(12) Wang, H. P.; Yates, J. T. *J. Phys. Chem.* **1984**, *88*, 852.

0002-7863/91/1513-2919$02.50/0