

Figure 1. Pictorial view of the $[H_2W_{12}O_{42}]^{10-}$ molecule ion, showing location of the central H atoms.

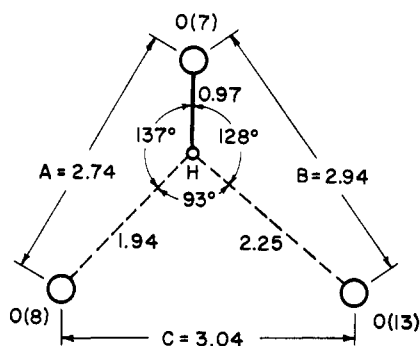


Figure 2. Projection of the four central atoms H, O(7), O(8), and O(13) onto the plane of the three oxygen atoms, showing interatomic distances in Å and angles at the H atom. Estimated errors of distances are ± 0.03 Å for O-O, ± 0.05 Å for O-H.

the overall structure will be published elsewhere.

We found that large crystals of $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$ (no. 2 above) suitable for neutron diffraction study can be readily obtained by slow evaporation of a saturated solution of the salt at $85^\circ C$. A stout prismatic crystal, $1.5 \times 2 \times 3$ mm, was used for diffraction measurements. The unit cell is monoclinic, space group $P2_1/n$, with $a = 15.079$ (2) Å, $b = 14.450$ (2) Å, $c = 10.968$ (1) Å, $\beta = 109.24$ (1)°, and $Z = 2$ (dimensions obtained by least-squares refinement from X-ray powder data measured by the Guinier-Hägg method). Data were collected at the National Bureau of Standards research reactor with neutrons of wavelength 1.273 Å. Within the 2θ range of 15 to 118° , 1553 independent reflections were measured greater than $2\sigma(I)$, out of a possible 5256. Phases for the corresponding F values were calculated on the basis of the structure parameters obtained by D'Amour and Allmann.² The F Fourier synthesis calculated with this data set revealed the positions of all 25 H atoms in the asymmetric unit of the structure. In particular, the H atom within the molecule gave the sharpest and strongest image, at $x, y, z = -0.023, 0.068, 0.014$. Full anisotropic refinement of the structure (503 parameters) has converged at the conventional reliability indexes $R = 0.151$ and $R_w = 0.123$. The relatively high index values result from inadequate modeling of the NH_4 hydrogen atoms, which are subject to strong libration.

A pictorial view of the molecule, including the molecular H atoms as found in this study, is shown in Figure 1. The H atom is bonded to the central O(7) atom as predicted by D'Amour and Allmann.² Their suggestion that the OH bond is directed primarily toward O(8) is also generally confirmed. The H atom lies near to the plane defined by O(7), O(8), and O(13) at a distance of 0.10 Å (toward the molecular center), and the dimensions of the atomic arrangement projected onto this plane are shown in Figure 2. Although the hydrogen bond is most strongly directed toward O(8), it is clearly bifurcated and is also substantially involved with O(13). The distance between the two H atoms in the molecule

Table I

compd	A	B	C	esd (O-O)	ref
1	2.86	2.86	3.11	0.035	1
2	2.83	3.04	3.16	0.05	2
3	2.74	2.94	3.04	0.03	this work
4	2.89	2.96	3.17	0.05	3
5	2.85	3.08	3.20	0.04	4
6	2.81	3.03	3.16		
5	2.80	2.83	3.03	0.07	5
6	2.80	2.90	3.03	0.06	6
av	2.822	2.968	3.112		

is 2.14 (5) Å, in good agreement with the value of 2.22 (2) Å found from NMR measurements by Lunk et al.⁷

The disposition of the molecular H atoms also bears on the question as to whether the free molecule has $2/m$ or only $\bar{1}$ symmetry. Evans⁶ concluded from a comparison of W-W distances in five published structures that departures from $2/m$ symmetry do not appear to be systematic and could result from the surrounding asymmetry of cations and water molecules in the crystal structure. If the molecular H atoms are assumed to be essentially unaffected by the external environment of the molecule, there is now reason to postulate that its symmetry is inherently $\bar{1}$. Presumably the distortion is rooted in the disposition of the central H atoms, and so the dimensions of the oxygen triangle may be examined for a systematic trilinearity in other structures. These dimensions (in Å) for the measured molecules are set forth in Table I, referring to the compounds listed above, and in Figure 2. From these data, we may definitely conclude that the paradodecatungstate molecule has $\bar{1}$ (C_i) symmetry, at least in the crystal. However, the displacement of the nonlabile H atom from the pseudomirror plane is only ~ 0.1 Å, so that the atom can be expected to be easily shifted from one side to the other by modest external forces. Therefore, the free molecule in solution probably oscillates in this way, and would most likely have time-averaged symmetry of $2/m$ (C_{2h}).

Registry No. $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$, 11113-17-0.

Formation of Ozonides: A Kinetic Secondary Isotope Effect for the Carbonyl Oxide

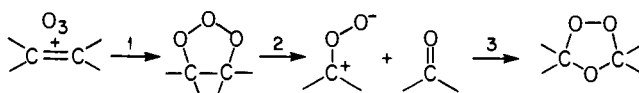
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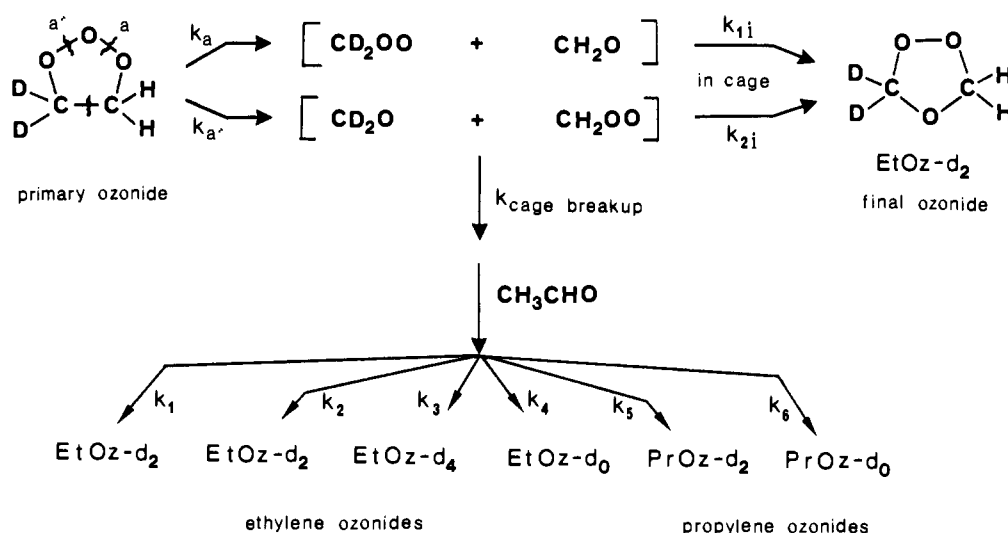
The ozonolysis of alkenes is usually described by the Criegee mechanism (Scheme I).¹ In recent stereochemical studies it was postulated that the reaction steps are concerted cycloadditions or cycloreversions.²⁻⁴ Considerable data support this conclusion for step 1.^{5,6} However, the evidence that steps 2 and 3 are

Scheme I



- (1) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.
- (2) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* **1974**, *96*, 348.
- (3) Bailey, P. S.; Ferrell, T. M. *J. Am. Chem. Soc.* **1978**, *100*, 899.
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- (5) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.
- (6) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

Scheme II



concerted is more indirect and results suggest nonconcerted processes for some conditions.^{7,8}

This communication provides evidence that an inverse deuterium kinetic secondary isotope effect (KSIE) can be associated with the carbonyl oxide H₂COO in step 3. This is the usual expectation when carbon transforms from nominal sp² to sp³ in the transition state.⁹ Since an inverse KSIE occurs for formaldehyde in step 3,^{10a} the results are consistent with both carbon centers participating in the transition state and supportive of a concerted cycloaddition, at least for small carbonyl oxides and aldehydes.

An indirect approach is necessary to probe a KSIE for H₂COO since it is too reactive for direct observation. Its properties are inferred from trapping experiments, and KSIE at all stages of the reaction must be considered. To explore this question, CH₂=CD₂ was ozonized in CHFCl₂ at -116 °C in the presence of variable amounts of CH₃CHO.¹³ This alkene eliminated complications from KSIE in steps 1 and 2 since CH₂OOCD₂ produces a 50/50 ratio of H₂COO/D₂COO.¹⁵ When CH₃CHO is present, the expected ozonide products are given by Scheme II.

Total ozonide yields varied from 70% to 80%. The ratio PrOz/(PrOz + EtOz) increased from 10/90 to 25/75 as [CH₃CHO] increased from 0.1 to 1.0 M. The yields of PrOz-d₀ and PrOz-d₂ revealed an interesting variation, shown in Table I.¹⁷

Table I. Propylene Ozonide (PrOz) Deuterium Content from Ozonolysis of CH₂CD₂/Acetaldehyde Mixtures

CH ₃ CHO, M	PrOz-d ₀ / (PrOz-d ₀ + PrOz-d ₂) × 100		
	obsd	calcd 1 ^a	calcd 2 ^a
0.10	52.7 ± 1.5 (3) ^b	52.8	47.5
0.25	49.7 ± 0.7 (3)	49.8	47.5
0.50	48.0 ± 1.0 (2)	47.8	47.5
1.00	46.3 ± 0.5 (2)	46.5	47.5

^a Calcd 1 assumes an inverse KSIE for the carbonyl oxides while calcd 2 does not; see text. ^b Number of data points in parentheses.

A computer algorithm was written to describe Scheme II and calculate the ratios PrOz/(PrOz + EtOz) and PrOz-d₀/(PrOz-d₀ + PrOz-d₂). The program assumed initial concentrations for CH₂OOCD₂ and CH₃CHO and relative rate constants. It differentiated between in-cage and out-of-cage EtOz formation and numerically calculated the ozonide yields until the carbonyl oxides were depleted. A wide variation in assumptions is possible, and the best agreement we have presently obtained is shown in Table I as calcd 1. Some of the salient assumptions include (1) 85% of the EtOz is formed outside the original solvent cage,^{10a} (2) CH₂O is 5 times more reactive than CH₃CHO (e.g., k₄ = 5k₆),¹⁸ and (3) the rate constants incorporate a KSIE of 0.7 for CD₂OO with formaldehyde, 0.6 for CD₂OO with acetaldehyde, and 0.7 for CD₂O with the carbonyl oxide (per D at -116 °C). The same model without the carbonyl oxide KSIE (calcd 2) gave a small excess of PrOz-d₂ over PrOz-d₀ but was insensitive to [CH₃CHO]. Both calculations reproduce PrOz/(PrOz + EtOz) to within 5% as [CH₃CHO] is varied. Examination of a more extensive set of calculations gives evidence that an inverse KSIE of 0.6–0.8 is associated with the carbonyl oxide in its reaction with the aldehydes. A KSIE in this range is common to those calculations that result in a variation in PrOz-d₀/(PrOz-d₂ + PrOz-d₀) similar to experiment.

A qualitative interpretation of the model calculations in Table I can be given. If CH₂OO and CD₂OO display no KSIE (calcd

(17) The mixture of ozonides was isolated by vacuum line techniques. Manometric measurements and ¹H NMR of the mixture provided sufficient data to determine the ratios in the text.^{10b} The amount of ethylene ozonide (EtOz) was also estimated by NMR by assuming the average hydrogen content in EtOz to be 2. The isotopic distribution among the three EtOz species cannot be obtained by proton NMR and other methods will be employed.

(18) See ref 10b for another example using numerical methods to rationalize yields from propylene ozonolyses and requiring CH₃CHO to be less reactive than H₂CO.

(7) Harding, L. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1978**, *100*, 7180.
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(9) Concerted cycloadditions typically exhibit inverse effects¹⁰ (k_H/k_D ≈ 0.80–0.95 at 25 °C). Nonconcerted processes and those developing a radical center at carbon often have normal or nearly normal isotope effects (k_H/k_D ≈ 0.97–1.20)^{10a,11} although exceptions are also found.^{11c,12}

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(12) (a) Baldwin, J. E.; Kapecki, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4874. (b) Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. *Ibid.* **1978**, *100*, 2570.

(13) The ozonolysis techniques^{2,10a,b} and the deuterium determination in ethylene¹⁴ have been described. All results are based on 100% CH₂=CD₂.

(14) Larrabee, A. L.; Kuczkowski, R. L. *J. Catal.* **1978**, *52*, 72.

(15) This ratio (±2%) was found for trapping experiments with MeOH in CHFCl₂ (1:3 ratio) by using NMR¹⁶ and presumably also applies to ozonolyses in the presence of acetaldehyde.

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2), their reactions with CH_3CHO lead to $\text{PrOz-}d_0/(\text{PrOz-}d_2 + \text{PrOz-}d_0) < 0.5$. The deviation below 0.5 develops because the in-cage recombination of $\text{D}_2\text{CO} + \text{H}_2\text{COO}$ is favored due to the KSIE for D_2CO .^{10a} This leads to $[\text{D}_2\text{COO}] > [\text{H}_2\text{COO}]$ in reactions with CH_3CHO . If an inverse KSIE also promotes the reactivity of D_2COO (calcd 1) and if $[\text{CH}_3\text{CHO}]$ is low, then the faster reactions that produce EtOz over PrOz lead to $[\text{H}_2\text{COO}] > [\text{D}_2\text{COO}]$ and $\text{PrOz-}d_0 > \text{PrOz-}d_2$. However, as $[\text{CH}_3\text{CHO}]$ increases, the formation of PrOz becomes more competitive with EtOz. In that case more PrOz- d_2 than PrOz- d_0 is produced since a larger proportion of PrOz formation occurs when $[\text{CH}_2\text{OO}]$ and $[\text{CD}_2\text{OO}]$ are more nearly equal.

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Registry No. Ethylene, 74-85-1; acetaldehyde, 75-07-0; formaldehyde, 50-00-0; deuterium, 7782-39-0.

Deuterium NMR Study of Organic Molecules Absorbed by Zeolites[†]

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Measurement of deuterium NMR spectra has recently been used to study molecular motion in solids.¹ The deuterium quadrupole interaction usually dominates the nuclear spin internal Hamiltonian so that the powder pattern resonance line shapes obtained can be a critical test for models of molecular motion. Also, the rigid-lattice quadrupole splittings are usually less than a few hundred kilohertz and can be observed by use of the quadrupolar spin echo.² In this communication, the first measurement of deuterium spectra of labeled organic molecules adsorbed within the internal channels of a zeolite molecular sieve is presented. In crystalline zeolites, the organic adsorbate can have highly restricted reorientational motion and slow translational diffusion.³ Observation of the deuterium spectrum offers new and direct information on the dynamics of organic molecules within zeolitic materials.

Deuterium spectra were obtained on a Bruker SXP-100 operating at $\omega_0/2\pi(^2\text{H}) = 13.82$ MHz. The synthetic zeolite ZSM-5 was prepared in the hydrogen form with calcination at 550 °C and outgassed at 400 °C in the NMR tube for several hours under vacuum. Loading of organic molecules was then performed by exposing the tube to the vapors over liquid per-deuterated *p*-xylene so that total absorption was 6.9% (w/w). Adsorption on external surfaces of the zeolite was found to be very small and details will be reported in a forthcoming paper.

The deuterium spectra of the absorbed *p*-xylene are shown in Figure 1. The half-spectra (nonquadrature) from Fourier transformation of the quadrupolar echo decay are illustrated at three temperatures. The striking result is that a broad powder pattern spectrum is obtained at all temperatures indicated. These spectra arise from *p*-xylene molecules with highly restricted reorientational motion within the molecular sieve.

[†] Contribution No. 3229.

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(2) Davis, J.; Jeffrey, K.; Bloom, M.; Valic, M.; Higgs, T. *Chem. Phys. Lett.* **1976**, *42*, 390.

(3) Breck, D. W. "Zeolite Molecular Sieves"; Wiley: New York, 1974.

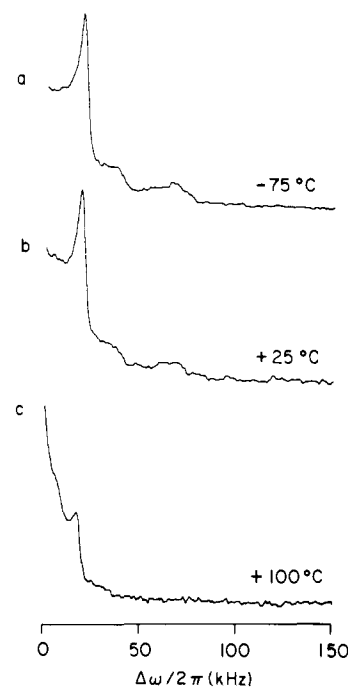


Figure 1. Deuterium NMR spectra of per-deuterated *p*-xylene adsorbed by zeolite ZSM-5. Broad powder pattern spectra due to the deuterium quadrupole interaction are obtained. This results from the restriction of the motion of *p*-xylene by the molecular sieve. The methyl group peak and pedestal are clearly visible having $\omega_Q/2\pi = 35$ kHz. The aromatic site produces a broad, rigid-lattice type spectrum at room temperature and below, having $\omega_Q/2\pi = 124$ kHz. The aromatic powder pattern is motionally narrowed at 100 °C. The vertical scale of c is reduced from that of a and b.

In Figure 1 a and b, the spectra obtained for *p*-xylene are characteristic of rigid-lattice molecular sites found in solids. The symmetric powder pattern arising from the methyl groups is clearly visible and gives $\omega_Q/2\pi = (3/4)e^2qQ = 35$ kHz. We obtain the same value for ω_Q from neat polycrystalline *p*-xylene at -75 °C. A smaller peak that we assign to the *p*-xylene aromatic deuterons appears at larger offset frequency. Taking this as the singular peak in the aromatic deuteron powder pattern gives $\omega_Q/2\pi = 124$ kHz. A sharper peak having about the same relative intensity was obtained for neat polycrystalline *p*-xylene, giving $\omega_Q/2\pi = 126$ kHz.

In Figure 1c, the spectrum of the same sample at +100 °C is shown. The powder pattern of the methyl groups is nearly unchanged. However, the broad component seen at lower temperatures has disappeared and a narrower resonance is found with a shoulder at 8.3-kHz offset. From this spectrum it is apparent that the motion of *p*-xylene molecules is restricted by the molecular sieve even at temperatures approaching those used for commercial reactions.

The spin-lattice relaxation times for the resonance shown in Figure 1 were less than 1 s in all cases. In neat, polycrystalline *p*-xylene the methyl group T_1 , was about 2 s and the aromatic group T_1 was at least 100 s.

From the line-shape and relaxation data, the dynamics of the *p*-xylene reorientation can be investigated. At the high temperature (100 °C), the resonance arising from the aromatic site is evidently motionally narrowed, but the methyl resonance is not. Considering the symmetry of the molecule and the known rotation of the methyl group about its C_3 axis, this can happen if the *p*-xylene molecule can reorient about an axis that passes through the C_3 axes of the para-methyl groups. For the simplest model of free rotation about that axis, a symmetric powder pattern would result for the aromatic site with its singular peak at $\frac{1}{2}[3 \cos^2(60) - 1]124 = 7.8$ kHz. This value is close to the position of the shoulder in Figure 1c. A portion of the narrow resonance at zero offset probably arises from molecules forced out of the zeolite