sum of the molecular orbital energies, Politzer and Parr[26] have shown that the total energy can also be expressed exactly as the sum of atomic-like energies in which each term is a functional of the electronic density about the corresponding nucleus. This relationship was further discussed by Politzer, Daiker, and Trefonas[27] and Politzer[28] in subsequent studies, demonstrating that the total energy of a molecule can be expressed in terms of a property evaluated at its nuclei. From the observed experimental correlation, one can speculate that, as substituents are introduced into the ring structure, the molecular and atomic contributions to the total energy change in a proportionate fashion. The molecular orbital energies would dictate the shifts in the optical spectrum while the atomic-like electrostatic potential of carbonyl carbon would determine the shifts in the NMR spectrum. It is intriguing that several groups have discussed a related correlation between the calculated diamagnetic shielding and electronic transitions through variations in the core ionization potentials of molecules (the chemical shift in ESCA).[29] This relationship is said to exist because both $\sigma_d$ and core electron binding energies depend upon changes in the electrostatic potential at the nucleus due to the valence electrons.

It is well-known that there are unexplained analogies between $^1H$ and $^{13}C$ NMR chemical shifts for significant numbers of organic structures.[30,31] These similar trends in chemical shifts are theoretically quite puzzling since the contribution to the $^1H$ chemical shift is generally accepted to arise purely from diamagnetic contributions due to the hydrogen atom's lack of low-lying p orbitals and its high electronic excitation energies. Yet differences in $^1H$ chemical shifts of diastereotopic protons follow closely the $^{13}C$ shift differences in diastereotopic methyl groups, which suggests a common origin for the two as discussed by Eliel et al.[30] In light of the present results, it seems reasonable that the $^{13}C$ diamagnetic shielding could be responsible for this experimental connection with the $^1H$ shielding.

While the diamagnetic contribution relies upon changes in the ground-state wave functions only, perhaps accounting for the correlation's insensitivity to solvent effects on the 3s state, this explanation would also suggest that the normally dominant paramagnetic shielding term is either invariant or variant in a regular fashion. This is a possibility since the n → π* transition remains practically constant for the group of structures within each ring size. There are, however, other factors involved in $\sigma_p$ contribution, and it would seem an oversimplification to suggest that this was actually the case. Combinations of multiple contributions as well as long-range effects are also possible explanations but these have not yet been investigated.

## Conclusions

We have demonstrated that a very subtle aspect of the $^{13}C$ NMR chemical shift of carbonyl compounds correlates with the high-resolution n → 3s optical transition energy. The $1/\Delta E$ term in the paramagnetic shielding contribution has been considered as the possible basis for the correlation, although the transition symmetry is not one which would be expected to contribute to the $\sigma_p$ term, and significant solution-phase perturbations to the Rydberg state tend to weaken the support for this rationale. Diamagnetic shielding contributions have also been examined, and the results suggest that the basis of the optical and NMR chemical shift correlation is related to changes in the ground-state wave functions, exclusively. This rationalization is as follows: as substituents are introduced into the ring structure, the molecular and atomic contributions to the total energy change in a proportionate fashion. The diffuse molecular orbital energies would dictate the shifts in the optical spectrum while the atomic-like electrostatic potential of carbonyl carbon would determine the shifts in the NMR spectrum. It would be interesting to further investigate this possible explanation by studying the ESCA peak shifts of the carbonyl carbon in methyl isomers of cyclic ketones since the core binding energies in some type of molecules have been shown to be related to their respective diamagnetic shielding.

There are several implications of this experimental correlation. First, high-resolution optical spectroscopy may prove to be a useful technique in gaining insight into the nature of the chemical shift. Also, the possible connection between the NMR shifts and ground-state steric energies, such as the van der Waals interactions described by Chesnut, could extend the usefulness of $^{13}C$ shielding measurements. The application of this experimental finding to other functional groups is currently in progress.

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# Combined $^2H$ and $^{18}O$ Isotope Effects in Support of a Concerted, Synchronous Elimination of Acetaldehyde from a Bis(benzyl ethyl ether) Radical Cation

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**Abstract:** No evidence has been found of "hydrogen scrambling" accompanying decomposition of the benzyl ether molecular ion at times approaching 100 μs. Isotope effects upon product ion abundances have been measured for elimination of acetaldehyde from the molecular ions of multiply labeled diethoxyxylenes and compared with the results of calculations of kinetic isotope effects using the quasi-equilibrium theory. It is concluded that this rearrangement involving a 6-membered cyclic transition state can be described as a concerted, synchronous process.

A few years ago, we reported in a preliminary communication $^2H$ and $^{18}O$ isotope effects manifested in the unimolecular elimination of acetaldehyde from α,α′-diethoxy-*p*-xylene (I) and proposed this decomposition to be a concerted, synchronous re-

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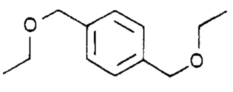
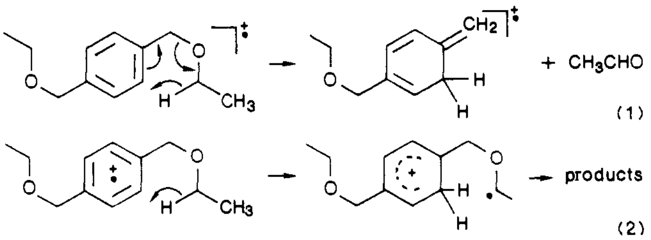


I

action[3] (see eq (1)). McLafferty et al.[4] have proposed that the same reaction proceeds in the benzyl ethyl ether radical cation in a stepwise manner via a distonic ion intermediate (see (2)).



In this paper, we examine this difference of opinion, in light of fresh evidence concerning kinetic isotope effects in multiply labeled isotopomers of I. The significance of the mechanism of this reaction stems from the likelihood, in our view, that this does indeed constitute an example of a concerted, synchronous reaction. The prevailing view has been for a number of years that the McLafferty rearrangement[5] in aliphatic aldehyde,[6] ketone,[7] and carboxylic acid[8] radical cations occurs in a stepwise fashion, and, especially recently given the upsurge of interest in distonic ions,[9] there has been a tendency to assume that in the absence of evidence to the contrary all such rearrangements of radical cations involving 6-membered cyclic transition states are adequately described by stepwise mechanisms. From the broader viewpoint, the reaction assumes significance in light of the recently formulated role that synchronous multibond reactions are normally prohibited.[10]

In the communication[3] we reported that the elimination of acetaldehyde from the molecular ion of the diether I was not accompanied by "hydrogen scrambling". This would distinguish this rearrangement from many McLafferty-type rearrangements, since typically McLafferty rearrangements in the microsecond time frame are accompanied by a significant degree of hydrogen scrambling.

McLafferty et al.[4] reported that both $C_2H_4O$ and $C_2H_3DO$ were lost from the molecular ion of the specifically labeled benzyl ether $C_6H_5CH_2OCD_2CH_3$. The abundance ratio $[M - C_2H_4O]^{\bullet+}/[M - C_2H_3DO]^{\bullet+}$ was 0.024 for unimolecular decomposition at 25 μs and 0.10 at 50 μs. We have made similar measurements on this benzyl ether and have not found evidence of hydrogen exchange (vide infra).

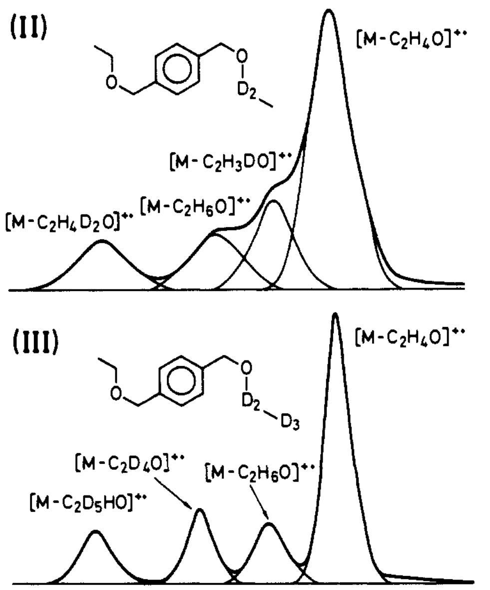


Figure 1. Regions of the mass-analyzed ion kinetic energy spectra of the molecular ions of the α,α′-diethoxy-*p*-xylenes II ($D_2$) and III ($D_5$).

Table I. Measured Ion Abundance Ratios

| compd<br>fragment ions | abundance ratio<br>measd | <br>corrcd[a] | %<br>confidence<br>limit |
|---|---|---|---|
| II ($D_2$) $[M - C_2H_4O]^{\bullet+}/[M - C_2H_3DO]^{\bullet+}$ | 3.33 ± 0.19 | 3.28 ± 0.19 | 99.5 |
| III ($D_5$) $[M - C_2H_4O]^{\bullet+}/[M - C_2D_4O]^{\bullet+}$ | 3.61 ± 0.07 | 3.41 ± 0.07 | 99.9 |
| IV ($^{18}O$) $[M - C_2H_4O]^{\bullet+}/[M - C_2H_4{}^{18}O]^{\bullet+}$ | 1.12 ± 0.07 | 1.09 ± 0.07 | 99.9 |
| V ($^{18}O,D_{10}$) $[M - C_2D_4O]^{\bullet+}/[M - C_2D_4{}^{18}O]^{\bullet+}$ | 1.09 ± 0.05 | 1.06 ± 0.05 | 99.9 |

[a] Correction has been made for efficiency of transmission through the mass spectrometer (see ref 14).

## Experimental Section

Measurements were made on a large double-focusing mass spectrometer of "reversed" geometry;[11] i.e., ions pass through the magnet before the electric sector. Mass-analyzed ion kinetic energy (MIKE) spectra were obtained by sweeping the potentials on the electric sector (radius 1000 mm). Molecular ions were formed by electron ionization at 70 eV and in some cases by field ionization. Spectra were recorded in both analog and digital modes.

Syntheses of the labeled ethers were carried out as follows. α-Ethoxy-α″([1,1-$^2H_2$]ethoxy)-*p*-xylene (II) and α′-([$^{18}O$]ethoxy)-*p*-xylene (IV) were made by similar procedures of which the following is typical. To a solution of sodium (115 mg) in anhydrous ethanol (1 mL) at 20 °C under nitrogen was added 1,4-bis(bromomethyl)benzene[12] (1.1 g) in ethanol (2 mL). The mixture was stirred at reflux for 2.25 h, poured onto water (20 mL), and extracted with diethyl ether (3 × 5 mL). The organic extract was washed with aqueous sodium chloride (saturated, 10 mL) and dried ($MgSO_4$), and the solvent was removed to give a colorless oil (910 mg). The oil was chromatographed on silica preparatory plates (2 × 35 g of $SiO_2$) in diethyl ether/light petroleum ether (40–50 °C) (1:4). Extraction of the central band with dichloromethane gave 1-(bromomethyl)-4-(ethoxymethyl)benzene as a colorless oil (435 mg, 46% yield). Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.4; H, 5.7. Found: C, 52.5; H, 5.6. Reaction of 1-(bromomethyl)-4-(ethoxymethyl)benzene (100 mg) with sodium and [$^{18}O$]ethanol (as above), 1-(ethoxymethyl)-4-([$^{18}O$]ethoxymethyl)benzene (IV) as a colorless oil (54 mg, 62% yield; $^{18}O$ = 10.4).

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(12) Wenner, W. *J. Org. Chem.* **1952**, *17*, 523. This method gives a mixture of dibromo and tribromo compounds. We could only obtain pure 1,4-bis(bromomethyl)benzene by repeated crystallization from ethanol (yield 18%).

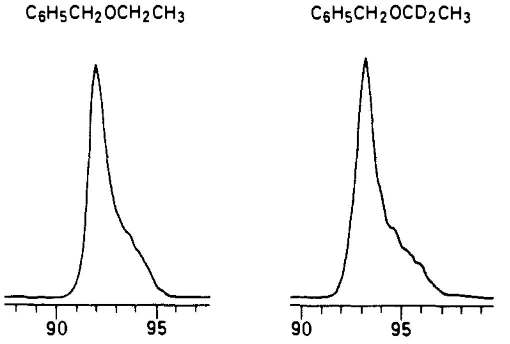

**Figure 2.** Regions of the mass-analyzed ion kinetic energy spectra of the molecular ions of benzyl ethyl ether and benzyl [1,1-$^2H_2$]ethyl ether.

α-([1,1,2,2,2-$^2H_5$]Ethoxy)-α′-([1,1,2,2,2-$^2H_5$,$^{18}O$]ethoxy)-*p*-xylene (V) was made as follows. To a stirring mixture of sodium hydride (60% in oil, 68.5 mg), tetrahydrofuran (1.5 mL), and [$^2H_5$, $^{18}O$]ethanol (100 μL, from iodoethane-$d_5$ and $D_2{}^{18}O$ ($^{18}O$ = 20.8%)[13]) at 20 °C under nitrogen was added 1,4-bis(bromomethyl)benzene (206 mg) in anhydrous dimethylformamide (10 mL). The mixture was stirred at 20 °C for 3.5 h, poured into water (50 mL), filtered through Celite, and extracted with diethyl ether (3 × 10 mL). The organic extract was washed with aqueous sodium chloride (15 mL) and dried ($MgSO_4$), and the solvent was evaporated to give an oil (175 mg). This oil was chromatographed (as above) on silica to give the isotopic mixture of bis(ethoxymethyl)benzenes as a colorless oil (97 mg, 61%), which was then fractionated (T-tube). The purity of this material was confirmed by mass spectrometry (MS), $^{13}C$ NMR, and gas chromatography. Statistically, the reaction should give the following isotopically labeled compounds: ($D_{10}$, $^{16}O_2$):($D_{10}$, $^{16}O_1$, $^{18}O_1$):($D_{10}$, $^{18}O_2$) = 64:32:4 [found (MS) 62:33:5].

## Results

Mass-analyzed ion kinetic energy (MIKE) spectra were obtained for the molecular ions of α,α′-diethoxy-*p*-xylene (I) and four of its isotopomers: α-ethoxy-α′-([1,1-$^2H_2$]ethoxy)-*p*-xylene (II), α-ethoxy-α′-([1,1,2,2,2-$^2H_5$]ethoxy)-*p*-xylene (III), α-ethoxy-α′-([$^{18}O$]ethoxy)-*p*-xylene (IV), and α-([1,1,2,2,2-$^2H_5$]ethoxy-α′-[(1,1,2,2,2-$^2H_5$,$^{18}O$]ethoxy)-*p*-xylene (V). The unlabeled molecular ion's MIKE spectrum contains peaks corresponding to loss of $C_2H_4O$ and to loss of $C_2H_6O$. The equivalent regions of the MIKE spectra of the molecular ions of two of the isotopomers are shown in Figure 1. In order to estimate relative ion abundances, it was necessary to perform peak subtraction in all cases except the $D_5$ species, III. It was assumed that peaks due to elimination of acetaldehyde from a given molecular ion had similar shapes to each other and likewise that peaks due to ethanol loss were similar to each other. Isotope effects on ethanol loss were assumed to be negligible. The uncertainties given (Table I) do, however, include allowance for the possibility of isotope effects upon ethanol loss. Note that there was no loss of $C_2D_6{}^{18}O$ from the molecular ion of V. All MIKE spectra have been measured a number of times and on a number of different occasions over a period of several years. The ion abundance ratios were corrected to allow for transmission losses stemming from energy released during decomposition.[14] The results are shown in Table I. Abundance ratios were estimated both on the basis of peak area and on the basis of peak height, and differences between the methods are reflected in the uncertainties given[15] (Table I).

A small region of the MIKE spectrum of the molecular ion of benzyl ethyl ether is shown in Figure 2, together with the corresponding region of the MIKE spectrum of the molecular ion of benzyl [1,1-$^2H_2$]ethyl ether. The accelerating potential was 2 kV in each case, which corresponded to a time window of 37–88 μs in the case of the deuteriated molecular ion.

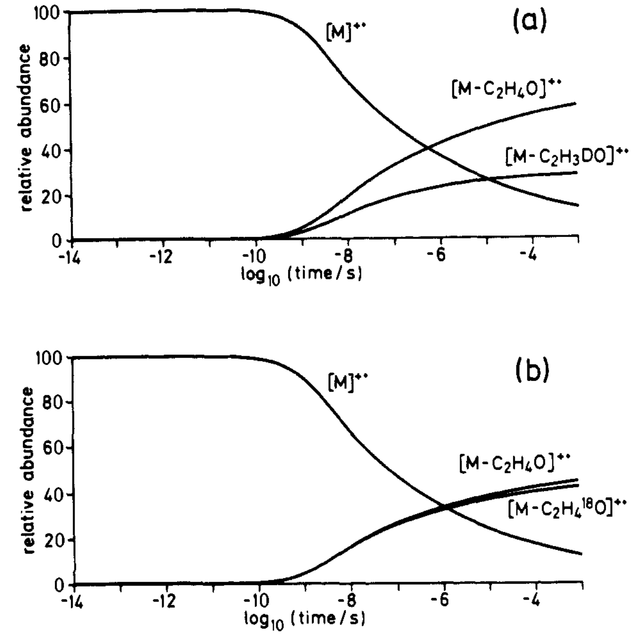

**Figure 3.** Calculated relative ion abundances as a function of time for the α,α′-diethoxy-*p*-xylenes II ($D_2$), and IV ($^{18}O$) assuming a concerted synchronous mechanism.

Photoionization[16] was used to measure the ionization energy (IE) of α,α′-diethoxy-*p*-xylene (I) and the appearance energy (AE) of the fragment ion due to acetaldehyde loss. The IE and AE were 8.42 ± 0.02 and 9.16 ± 0.10 eV, respectively. From these figures, the critical energy for acetaldehyde loss is 0.74 ± 0.12 eV (71.2 ± 12.0 kJ $mol^{-1}$).

Modeling of the loss of acetaldehyde from the molecular ions of the α,α′-diethoxy-*p*-xylene (I–toV) was carried out by statistical rate theory (quasi-equilibrium theory (QET) or Rice–Ramsperger–Kassel–Marcus (RRKM) theory)[17] to calculate microcanonical rate constants $k(E)$. Our aim was to evaluate the two published proposals,[3,4] namely that the reaction is concerted and synchronous as opposed to the reaction being stepwise via an intermediate in a deep well (the "two barriers of similar height" proposal). Vibrational frequencies for the molecular ions of I and its isotopomers (II–V) were obtained by calculation, using a semiempirical molecular orbital package (MOPAC).[18,19] For

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[13] Murray, A.; Williams, D. L. *Organic Syntheses with Isotopes*; Interscience: New York, 1958; Part II, p 1330.

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[15] The abundance ratios represent the relative abundances of the isotopomeric fragment ions formed in time windows extending from 2 × $10^{-5}$ to 5 × $10^{-5}$ s. The uncertainties arise in large part from differing source conditions on different occasions and from differences between peak areas and peak heights.

[16] Measurements were made at La Trobe University by Dr. J. C. Traeger. For a description of the technique, see: Traeger, J. C.; McLoughlin, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *27*, 319.

[17] The expression $k(E) = G^*(E - E_0)/(hN(E))$ was evaluated exactly by means of direct counting of states. $k(E)$ is the microcanonical rate constant, $G^*(E - E_0)$ is the number of states in the transition state, and $N(E)$ is the density of states in the reactant. See: Forst, W. *Theory of Unimolecular Reactions*; Academic: New York, 1973. The algorithm employed to count states and the computer programs have been described: Allison, C. E. Ph.D. Thesis, University of New South Wales, 1986. (Copies of this thesis are available upon request from the Librarian, University of New South Wales, P.O. Box 1, Kensington, NSW 2033, Australia.) This expression for the microcanonical rate constant $k(E)$ was derived independently at about the same time by Rosenstock et al. (Rosenstock, H. M.; Wallenstein, M. B.; Wahrhaftig, A. L.; Eyring, H. *Proc. Natl. Acad. Sci.* U.S.A. **1952**, *38*, 667) and by Marcus (Marcus, R. A. *J. Chem. Phys.* **1952**, *20*, 359). Applied in a straightforward fashion, the absolute values of rate constants calculated using the expression have been shown to be in satisfactory agreement with experiment for a variety of large organic ions and $k(E)$'s in the range $10^4$–$10^7$ $s^{-1}$. See, for example: Baer, T.; Willett, G. D.; Smith, D.; Phillips, J. S. *J. Chem. Phys.* **1979**, *70*, 4076.) Our application is less demanding of the theory, because the concern is with relative rates and with parallel reactions of a single reactant occurring over identical potential energy surfaces. This places constraints upon adjustments of vibrational frequencies and critical energies. For a discussion, see: Derrick, P. J.; Donchi, K. F. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, the Netherlands, 1983; Vol. 24, pp 53–247.

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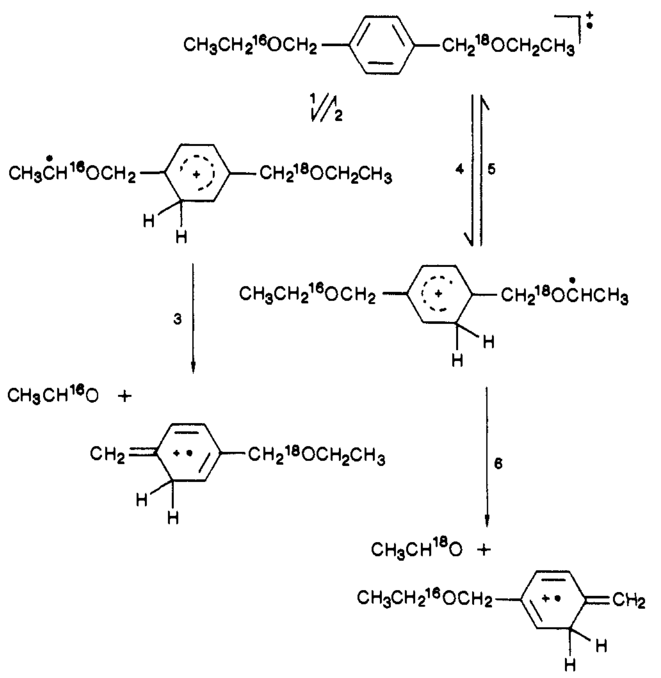
**Scheme I**



the concerted mechanism, the critical energy in the case of I was considered to lie between 59 and 83 kJ mol$^{-1}$. The effects upon the calculated rate constants $k(E)$ of varying the critical energy within this range were investigated systematically for different transition-state models. Results are presented for simpler transition-state models. Dependences upon time of abundances of molecular and product ions were obtained from rate constants $k(E)$ by means of the expression (3).[20]

$$\text{rate} = \int_0^{E_{\max}} k_1(E)\, P(E)\, \exp\Bigl(-\sum_{i=1}^{n} k_i(E)t\Bigr)\, \mathrm{d}E \tag{3}$$

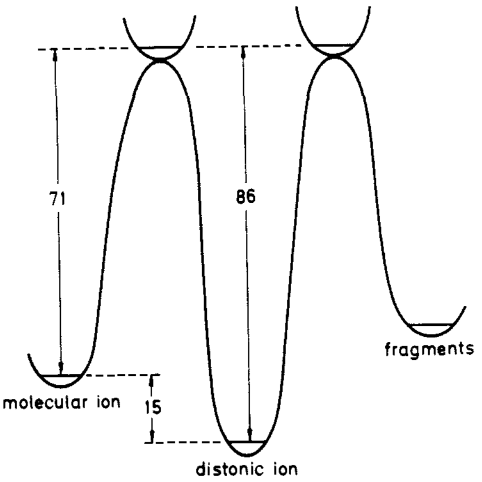


Figure 4. Energies of the $\alpha,\alpha'$-diethoxy-$p$-xylene molecular ion, its distonic ion, the products of the McLafferty rearrangement, and the transition states, as used in calculating the results shown in Figure 5.

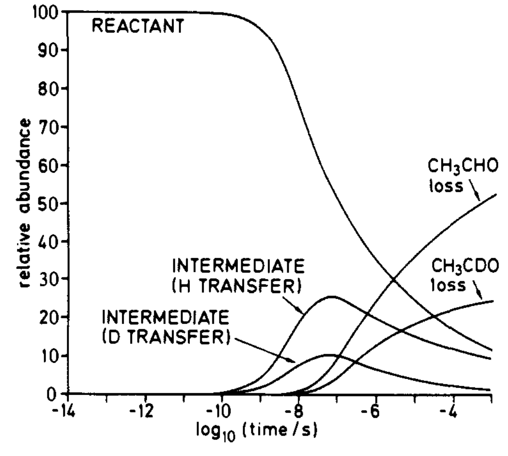


Figure 5. Calculated relative ion abundances as a function of time for the $\alpha\alpha'$-diethoxy-$p$-xylene II ($D_2$), assuming a stepwise mechanism.

At reaction times as lengthy as 20–50 μs, the calculated ratios of the abundances of the isotopomeric product ions (e.g. $[M - C_2H_4O]^{\bullet+}/[M - C_2H_3DO]^{\bullet+}$ from the molecular ion of II were highly sensitive to differences between their critical energies. When the experimental value of 71 kJ mol$^{-1}$ for the critical energy is used (in the case of the unlabeled molecule I) and a reactant-like transition state[21] is taken, the dependences of ion abundances upon time shown in Figure 3 were obtained. The isotopomeric abundance ratios for products formed in the time windows of the MIKE experiments were 3.29, 3.46, 1.08, and 1.07 for $[M - C_2H_4O]^{\bullet+}/[M - C_2H_3DO]^{\bullet+}$ (from II), $[M - C_2H_4O]^{\bullet+}/[M - C_2D_4O]^{\bullet+}$ (from III), $[M-C_2H_4O]^{\bullet+}/[M - C_2H_4{}^{18}O]^{\bullet+}$ (from IV), and $[M - C_2D_4O]^{\bullet+}/[M - C_2D_4{}^{18}O]^{\bullet+}$ (from V), respectively (cf. 3.28, 3.41, 1.09, and 1.06 (Table I)). In this calculation, the precise critical energies employed for $C_2H_4O$ and $C_2H_3DO$ loss in the case of II were 71.17 and 74.11 kJ mol$^{-1}$, respectively; those for $C_2H_4O$ and $C_2D_4O$ from III were 71.17 and 74.34 kJ mol$^{-1}$, respectively; those for $C_2H_4O$ and $C_2H_4{}^{18}O$ from IV were 71.17 and 71.37 kJ mol$^{-1}$, respectively; and those for $C_2D_4O$ and $C_2D_4{}^{18}O$ from V were 74.34 and 74.51 kJ mol$^{-1}$, respectively. If the transition states were "tightened" so that $k(E)$'s rose more slowly

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(19) The vibrational frequencies of the molecular ions of $\alpha,\alpha'$-diethoxy-$p$-xylene (I) and its isotopomers (II–V) were as follows. I (Unlabeled): 36, 36, 36, 36, 44, 70, 77, 78, 142, 146, 149, 212, 251, 253, 285, 323, 352, 419, 420, 478, 536, 540, 639, 719, 791, 792, 793, 806, 834, 881, 887, 921, 921, 928, 934, 949, 970, 1050, 1051, 1076, 1077, 1088, 1115, 1116, 1152, 1154, 1157, 1157, 1202, 1205, 1223, 1257, 1272, 1279, 1288, 1293, 1294, 1294, 1294, 1304, 1309, 1310, 1314, 1335, 1337, 1338, 1355, 1360, 1367, 1373, 1378, 1479, 2858, 2858, 2867, 2867, 2916, 2917, 2920, 2920, 2948, 2949, 2950, 2953, 3014, 3016, 3038, 3039, 3048, 3052. II ($D_2$): 36, 36, 36, 36, 42, 70, 77, 78, 140, 145, 148, 211, 248, 252, 285, 320, 352, 414, 419, 476, 536, 540, 638, 659, 718, 791, 793, 806, 833, 846, 870, 881, 887, 921, 926, 930, 934, 947, 969, 978, 1007, 1051, 1076, 1088, 1116, 1123, 1139, 1153, 1155, 1157, 1203, 1222, 1227, 1258, 1275, 1287, 1294, 1294, 1294, 1295, 1301, 1308, 1312, 1323, 1336, 1337, 1338, 1357, 1366, 1372, 1377, 1479, 2112, 2115, 2858, 2858, 2867, 2917, 2918, 2920, 2948, 2949, 2950, 2953, 3014, 3016, 3038, 3039, 3048, 3052. III ($D_5$): 36, 36, 36, 36, 41, 68, 74, 77, 110, 140, 147, 206, 248, 252, 285, 317, 349, 395, 419, 474, 532, 539, 585, 635, 717, 722, 791, 793, 805, 818, 835, 846, 867, 881, 887, 921, 925, 934, 943, 948, 955, 968, 970, 1013, 1051, 1076, 1088, 1116, 1123, 1152, 1154, 1156, 1157, 1203, 1221, 1224, 1258, 1275, 1287, 1294, 1294, 1301, 1308, 1312, 1322, 1336, 1337, 1357, 1365, 1372, 1377, 1479, 2111, 2114, 2160, 2177, 2179, 2858, 2858, 2867, 2917, 2918, 2920, 2949, 2952, 3015, 3038, 3039, 3048, 3052. IV ($^{18}O$): 36, 36, 36, 36, 44, 70, 75, 78, 141, 145, 149, 211, 250, 252, 285, 320, 352, 418, 419, 477, 535, 540, 639, 719, 791, 792, 793, 806, 834, 881, 887, 917, 921, 927, 934, 949, 969, 1050, 1051, 1076, 1077, 1088, 1114, 1116, 1152, 1153, 1155, 1157, 1185, 1203, 1223, 1256, 1265, 1276, 1287, 1293, 1294, 1294, 1294, 1303, 1306, 1310, 1313, 1335, 1337, 1337, 1346, 1355, 1360, 1370, 1377, 1479, 2858, 2858, 2867, 2867, 2916, 2917, 2920, 2920, 2948, 2949, 2950, 2953, 3014, 3016, 3038, 3039, 3048, 3052. V ($^{18}O,D_{10}$): 36, 36, 36, 36, 36, 66, 71, 74, 108, 111, 137, 199, 243, 249, 285, 309, 347, 389, 397, 468, 527, 538, 584, 585, 632, 716, 719, 723, 791, 804, 818, 818, 835, 846, 846, 865, 867, 881, 887, 923, 934, 941, 944, 948, 955, 955, 964, 968, 970, 1012, 1013, 1088, 1121, 1123, 1145, 1152, 1154, 1156, 1211, 1221, 1224, 1257, 1285, 1296, 1303, 1310, 1321, 1337, 1346, 1367, 1376, 1479, 2111, 2111, 2113, 2114, 2159, 2160, 2176, 2177, 2178, 2180, 2858, 2858, 2917, 2918, 3038, 3039, 3048, 3052.

(20) Derrick, P. J.; Donchi, K. F. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, tne Netherlands, 1983; Vol. 24.

(21) In every case, a C–O stretching frequency had been removed as the reaction coordinate (e.g. 1203 cm$^{-1}$ for loss of $C_2H_4O$ and 1155 cm$^{-1}$ for loss of $C_2H_3DO$ in the case of II). Six frequencies associated with the "active" ethyl group (two C–H (or C–D) stretches and four C–H (or C–D) bends) were lower (compared to the reactant) by 20%, two frequencies associated with the C–O–C linkage (one C–C bend and one C–O stretch) were lower by 55% and seven frequencies associated with the benzyl group (two C–H stretches, four C–H bends and one C–C stretch) were lower by 10%. All other frequencies were the same in the transition state as in the reactant.

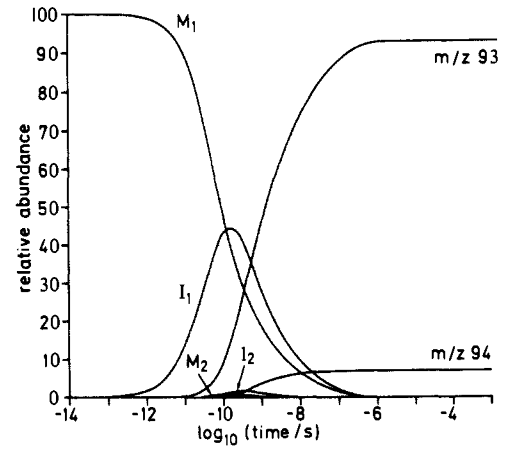


**Figure 6.** Calculated relative ion abundances pertaining to "hydrogen scrambling" in the benzyl $[1,1\text{-}^2H_2]$ethyl ether ion as a function of time.

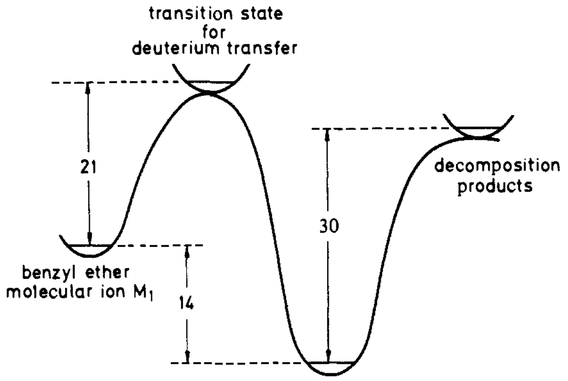
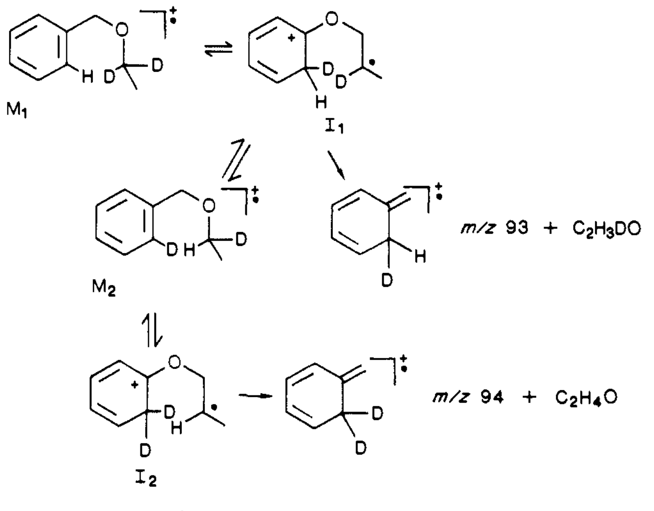


**Figure 7.** Energies of the benzyl $[1,1\text{-}^2H_2]$ethyl ether molecular ion, its distonic ion, the products of the McLafferty rearrangement, and the transition states, as used in calculating the results shown in Figure 6.

**Scheme II**



with *E*, the good fit of the calculated ion abundance ratios to the experimental values could be restored simply by lowering the critical energy (below 71 kJ $mol^{-1}$ in the case of I) and making slight adjustments to critical energy differences.

The type of kinetic scheme adopted in treating the stepwise mechanism is exemplified in Scheme I.[22] The reaction was considered to be *not* concerted, meaning that internal energy within the intermediates could be taken to be randomized prior to back-reactions to the molecular ions or forward reaction to eliminate acetaldehyde. The vibrational frequencies of the distonic ion intermediates were obtained by MOPAC calculations.[23] The MOPAC calculations gave the following heats of formation: $\Delta H_f$[molecular ion of I] ≈ 502 kJ $mol^{-1}$, $\Delta H_f$[unlabeled distonic ion] = 487 kJ $mol^{-1}$, $\Delta H_f$[products] = 512 kJ $mol^{-1}$. The values for the critical energies for forward and back hydrogen transfer and for C–O cleavage were varied systematically for a number of transition-state models, and dependences of ion abunances were calculated upon time. The metastable ion abundance ratios (Table I) could be approximated in quite a number of ways. When the critical energies shown in Figure 4 and simple transition-state models[25] were used, the dependences of ion abundances upon time

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(22) Using QET, microscopic rate constants *k*(*E*) were calculated as functions of the internal energy *E* of the reactant (molecular or appropriate distonic ion) for the six reactions in each case (formation of the distonic ions, back-reactions of the distonic ions to the molecular ion, and decompositions of the distonic ions to eliminate acetaldehyde). The abundances of the different species at time *t* are obtained by the method of Laplace transforms described in ref 27.

(23) The vibrational frequencies of the distonic ion intermediates were as follows. (a) Distonic ion formed from the molecular ion of I. 36, 36, 36, 36, 47, 50, 68, 98, 139, 150, 199, 215, 230, 248, 292, 329, 365, 399, 444, 465, 533, 561, 581, 707, 730, 771, 793, 797. 824, 869, 877, 894, 906, 910, 931, 936, 1035, 1038, 1052, 1061, 1063, 1076, 1077, 1115, 1116, 1145, 1154, 1159, 1195, 1223, 1233, 1241, 1253, 1259, 1272, 1279, 1285, 1292, 1296, 1296, 1297, 1301, 1302, 1310, 1326, 1337, 1341, 1361, 1388, 1411, 1431, 1679, 2850, 2870, 2875, 2890, 2909, 2920, 2926, 2933, 2933, 2938, 2946, 2950, 2957, 2997, 3014, 3047, 3062, 3065. (b) Two distonic ions in the case of II $(D_2)$. H transfer: 36, 36, 36, 36, 47, 50, 68, 98, 136, 149, 198, 214, 229, 246, 290, 328, 365, 399, 442, 461, 533, 561, 579, 661, 707, 730, 771, 797, 824, 851, 868, 872, 877, 896, 908, 915, 932, 935, 962, 1007, 1035, 1038, 1063, 1064, 1077, 1100, 1116, 1145, 1156, 1191, 1197, 1226, 1234, 1241, 1253, 1259, 1272, 1279, 1285, 1292, 1296, 1297, 1300, 1301, 1310, 1337, 1339, 1348, 1380, 1411, 1431, 1679, 2097, 2108, 2870, 2875, 2890, 2920, 2926, 2933, 2933, 2938, 2945, 2950, 2957, 2997, 3014, 3047, 3062, 3065. D transfer: 36, 36, 36, 36, 46, 50, 63, 97, 135, 146, 197, 212, 230, 247, 291, 326, 362, 392, 437, 464, 527, 546, 578, 687, 693, 719, 769, 793, 797, 812, 832, 851, 879, 900, 905, 931, 941, 951, 976, 1035, 1052, 1059, 1076, 1088, 1114, 1134, 1138, 1145, 1156, 1164, 1194, 1218, 1228, 1241, 1259, 1265, 1278, 1288, 1296, 1296, 1297, 1301, 1301, 1309, 1326, 1332, 1340, 1361, 1388, 1410, 1431, 1667, 2120, 2175, 2850, 2870, 2890, 2904, 2909, 2920, 2926, 2933, 2940, 2946, 2950, 2997, 3014, 3047, 3062, 3065. (c) III $(D_5)$. H transfer: 36, 36, 36, 36, 45, 50, 68, 96, 104, 147, 197, 212, 228, 237, 285, 327, 365, 397, 432, 455, 532, 559, 573, 587, 707, 716, 732, 772, 797, 822, 824, 847, 869, 871, 877, 896, 908, 915, 934, 946, 956, 962, 1011, 1035, 1038, 1063, 1064, 1077, 1103, 1116, 1145, 1157, 1195, 1203, 1224, 1233, 1241, 1253, 1259, 1272, 1279, 1285, 1292, 1300, 1301, 1310, 1337, 1347, 1378, 1411, 1431, 1679, 2096, 2108, 2159, 2174, 2178, 2870, 2875, 2890, 2920, 2926, 2933, 2933, 2938, 2957, 2997, 3047, 3062, 3065. D transfer: 36, 36, 36, 36, 44, 46, 57, 93, 135, 146, 193, 209, 228, 243, 289, 323, 362, 388, 428, 461, 525, 536, 576, 602, 684, 706, 715, 770, 793, 798, 811, 850, 853, 863, 880, 901, 905, 919, 929, 932, 941, 969, 1011, 1052, 1059, 1076, 1099, 1114, 1134, 1138, 1148, 1156, 1164, 1194, 1218, 1228, 1265, 1278, 1287, 1296, 1296, 1297, 1301, 1309, 1326, 1332, 1340, 1361, 1388, 1410, 1431, 1665, 2120, 2139, 2155, 2171, 2182, 2850, 2870, 2890, 2904, 2909, 2926, 2933, 2946, 2950, 3014, 3047, 3062, 3065. (d) IV $(^{18}O)$. $^{16}O$ reaction: 36, 36, 36, 36, 47, 50, 68, 98, 138, 149, 198, 213, 229, 246, 291, 327, 365, 399, 443, 463, 533, 560, 577, 707, 730, 771, 792, 797, 824, 869, 877, 893, 905, 909, 929, 935, 1035, 1038, 1052, 1060, 1063, 1076, 1077, 1113, 1116, 1145, 1153, 1157, 1195, 1209, 1231, 1241, 1253, 1259, 1272, 1279, 1284, 1290, 1294, 1296, 1296, 1301, 1301, 1310, 1315, 1337, 1339, 1352, 1371, 1411, 1431, 1679, 2850, 2869, 2875, 2890, 2909, 2920, 2926, 2933, 2933, 2938, 2946, 2950, 2957, 2997, 3014, 3047, 3062, 3065. $^{18}O$ reaction: 36, 36, 36, 36, 47, 50, 68, 97, 139, 150, 196, 213, 227, 247, 291, 327, 365, 399, 443, 533, 554, 580, 707, 730, 771, 793, 796, 824, 867, 877, 893, 905, 909, 931, 936, 1019, 1035, 1052, 1061, 1063, 1076, 1077, 1113, 1115, 1145, 1154, 1159, 1195, 1223, 1233, 1241, 1248, 1259, 1272, 1279, 1283, 1292, 1296, 1297, 1296, 1301, 1302, 1310, 1326, 1337, 1341, 1361, 1388, 1411, 1431, 1643, 2850, 2870, 2875, 2890, 2909, 2920, 2926, 2933, 2933, 2938, 2946, 2950, 2957, 2997, 3014, 3047, 3062, 3065. (e) V $(D_{10},{}^{18}O)$. $^{16}O$ reaction: 36, 36, 36, 36, 43, 45, 57, 92, 104, 138, 190, 205, 223, 229, 281, 319, 361, 387, 420, 440, 524, 533, 567, 586, 602, 683, 705, 711, 719, 770, 798, 811, 822, 846, 851, 853, 863, 869, 880, 901, 915, 920, 929, 939, 945, 956, 959, 969, 1009, 1012, 1061, 1099, 1102, 1133, 1138, 1148, 1161, 1193, 1197, 1213, 1221, 1265, 1278, 1288, 1300, 1308, 1331, 1335,1350, 1410, 1431, 1665, 2096, 2108, 2120, 2139, 2155, 2159, 2171, 2174, 2178, 2182, 2870, 2890, 2904, 2926, 2933, 3047, 3062, 3065. $^{18}O$ reaction: 36, 36, 36, 36, 43, 45, 57, 92, 104, 140, 188, 206, 221, 230, 281, 320, 361, 387, 422, 442, 522, 530, 570, 587, 599, 683, 705, 711, 721, 770, 797, 811, 822, 846, 851, 853, 862, 871, 880, 901, 915, 920, 929, 939, 946, 956, 963, 967, 995, 1011, 1061, 1094, 1103, 1133, 1139, 1142, 1162, 1193, 1203, 1218, 1229, 1265, 1278, 1288, 1300, 1308, 1331, 1346, 1378, 1410, 1431, 1628, 2096, 2108, 2120, 2139, 2155, 2159, 2171, 2174, 2178, 2181, 2870, 2890, 2904, 2926, 2933, 3047, 3062, 3065.

(24) Critical energies for H transfer: from close to 0 to 71 kJ $mol^{-1}$, for back-reaction of the intermediate from 0 to 86 kJ $mol^{-1}$ and for C–O cleavage from 0 to 86 kJ $mol^{-1}$ were considered.

shown in Figure 5 were obtained in the case of II. It is pointed out the abundances of the intermediates become significant at times shorter than 1 ns. The calculated metastable ion abundance ratios were 3.27, 2.89, 1.03, and 1.01 for the isotopomeric products from II–V, respectively; cf. experimental ratios 3.28, 3.41, 1.09, and 1.06, respectively. Changes to these critical energies (Figure 4) or transition-state models,[25] which gave increased values for the isotopomeric ratios calculated for IV and V, tended at the same time to produce falls in the ratio for (III) (see below). With the same transition-state models and the critical energy for hydrogen transfer as in Figure 4, lowering the critical energy for C–O cleavage caused the isotopomeric abundance ratios ($^{16}O/^{18}O$) for IV and V to fall below 1.00 (i.e. become inverse).[26] Tightening the transition state for hydrogen transfer to give a slower rise to $k(E)$ with $E$ tended to have the effect of raising the internal energies of ions decomposing in the 20–50-$\mu$s time window, and as a result the isotopomeric abundance ratios ($^{16}O/^{18}O$) for IV and V would tend to fall.

Hydrogen/deuterium exchange in the benzyl [1,1-$^2H_2$]ethyl ether molecular ion was investigated theoretically through a kinetic analysis of the reaction in Scheme II.

Using QET, rate constants $k(E)$ were calculated for the eight steps, and the relative abundances of the molecular ions $M_1$ and $M_2$, intermediates $I_1$ and $I_2$, and products were calculated as functions of time by solving the kinetic scheme in Scheme II with the method of Laplace transforms.[27] A range of values for the various critical energies and a number of different transition-state models were investigated. The results shown in Figure 6 were obtained with MOPAC energies for the different stable species ($M_1$, $M_2$, $I_1$, $I_2$, products) and the lowest possible critical energies (i.e. no reverse energy barriers) for C–O cleavages (see Figure 7). The critical energy for the initial D transfer ($M_1 \rightarrow I_1$) was 21 kJ mol$^{-1}$, and that for H transfer ($M_2 \rightarrow I_1$) was 16 kJ mol$^{-1}$.[28] Vibrational frequencies of the four reactants ($I_1$, $I_2$, $M_1$, and $M_2$) were obtained from MOPAC calculations.

The vibrational frequencies of a transition state for H or D transfer were obtained by averaging the frequencies of the molecular and distonic ion and removing a C–H(D) stretch as the reaction coordinate. The vibrational frequencies of a transition state for C–O cleavage were the same as those of the reactant distonic ion, except that a C–O stretch was used as the reaction. Results for these extremely simple transition states are reported (Figure 6), as the objective was to confirm the *relative* time scales for manifestation of hydrogen scrambling on the one hand and the establishment of significant relative abundances of intermediates on the other.

## Discussion

Whether or not acetaldehyde loss from the molecular ion of benzyl ether is accompanied by hydrogen scrambling is an important question in the present discussion, because hydrogen scrambling is quite often taken as a sign that a decomposition involves an intermediate. If hydrogen scrambling accompanied acetaldehyde loss from the benzyl ether ion, the proposition could be made with some confidence that this decomposition proceeds via an intermediate, that this intermediate is the distonic ion, and that by analogy loss of acetaldehyde from the molecular ion of $\alpha,\alpha'$-diethoxy-*p*-xylene proceeds via a distonic ion intermediate. It appears to be accepted[4] that there is no significant amount of hydrogen scrambling accompanying acetaldehyde loss from the benzyl ether ion at times of the order of 1 $\mu$s. The disagreement arises over the situation at longer times (approaching 100 $\mu$s). Figure 2 shows the peak at $m/z$ 92 attributed to loss of $CH_3CHO$ and the peak at $m/z$ 93 to loss of $CH_3CDO$ from the metastable molecular ions of benzyl ethyl ether and benzyl ethyl-*1,1-d*$_2$ ether, respectively, measured with an accelerating potential of 2 kV. This low accelerating potential, at which the resolution was degraded, was necessary in order that molecular ions with lifetimes in the range 40–90 $\mu$s decomposed in the second field-free region of the instrument. If the accelerating potential were raised to 10 kV, so that molecular ions with somewhat shorter lifetimes (factor of $\sqrt{5}$) were studied, the shoulders on both peaks largely disappeared. We interpret the shoulder on the $m/z$ 92 peak from the unlabeled molecular ion as fragment ions due to reaction pathways, which only become significant at these unusually long times. There would appear to be both a $m/z$ 93 and 94 peak, which presumably arise from loss of $C_2H_3O$ and $C_2H_2O$, respectively, either directly or indirectly from the benzyl ethyl ion. The area of the shoulder on the $m/z$ 93 peak from the $D_2$ molecule is approximately equal to that of the shoulder on the $m/z$ 92 peak. The shoulder on the $m/z$ 93 peak can be adequately explained as fragment ions formed by the reaction pathways, which in the unlabeled molecule affect loss of $C_2H_3O$ and $C_2H_2O$. Our conclusion is, therefore, that the MIKE spectrum of the benzyl ethyl-*1,1-d*$_2$ ether ion, which we have measured, provides no evidence of hydrogen scrambling accompanying acetaldehyde loss in the 40–90-$\mu$s time window.

It would generally be accepted that the distonic ion of the benzyl ether ion (see Scheme II) is a stable species in the sense of being a well on the potential energy surface.[9] MOPAC calculations indicate that this is the case.[27] McLafferty and co-workers[4] have concluded that the collisionally activated dissociation (CAD) spectrum of the $m/z$ 136 ion from benzyl ethyl ether is representative of the distonic ion rather than the molecular ion. Our kinetic analyses support the notion that isomerization of the molecular ion of benzyl ethyl ether to the distonic ion could proceed to the extent that a significant proportion of the $m/z$ 136 ions remaining undecomposed after $\mu$s had the distonic ion structure. This is evident from Figure 6. The analyses also predict, however, that the development of a significant abundance of the distonic ion should be accompanied by hydrogen scrambling on approximately the same time scale (as in Figure 6). By the same token, it can be inferred from the results (Figure 5) of the calculations on the diether molecular ions that, given a twin barrier/deep well mechanism, scrambling should be expected to occur in the microsecond time frame in this system also. That hydrogen scrambling is not observed in microseconds would according to our analyses be an indication that scrambling should not be expected at longer times.[29] Given that there is no hydrogen scrambling accompanying acetaldehyde loss in benzyl ethyl ether either at microseconds or at times approaching 100 $\mu$s, it is rea-

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[25] Vibrational frequencies for a transition state for hydrogen transfer were obtained by averaging corresponding pairs of vibrational frequencies of the molecular ion and the distonic ion, removing a C–H stretch as the reaction coordinate, and, for this particular calculation, lowering five (four C–H (or C–D) bends, one C–H (or C–D) stretch) of the constructed frequencies by 10%. For this particular calculation, the vibrational frequencies of a transition state for C–O cleavage were considered to be the same as those of the distonic ion, except for a C–O stretch removed as the reaction coordinate and seven frequencies (four C–H (or D) bends, two C–H (or D) stretches, one C–C stretch) lowered by 5% each.

[26] With $E_0$ for H transfer at 71 kJ mol$^{-1}$ and the reverse critical energy at 15 kJ mol$^{-1}$ (i.e. retaining the deep well), the calculated $^{16}O/^{18}O$ metastble ion ratio for (IV) is 0.97 if $E_0$ for C–O cleavage is 75 kJ mol$^{-1}$.

[27] Allison, C. E. Ph.D. Thesis, University of New South Wales, Australia, 1986.

[28] An appearance energy measurement by Dr. J. C. Traeger (see ref 16) gave 16 ± 5 kJ mol$^{-1}$ as the energy barrier to formation of $m/z$ 92 from benzyl ethyl ether, which is to be compared with the corresponding figure for the diether of 71 ± 12 kJ mol$^{-1}$ (see ref 16).

[29] See: Derrick, P. J.; Falick, A. M.; Burlingame, A. L.; Djerassi, C. *J. Am. Chem. Soc.* **1974**, *96*, 1054, 1059. The stabilization of the distonic ion intermediate in the Mclafferty rearrangement in a ketone shifts "hydrogen scrambling" to shorter times (nanoseconds) rather than to longer times.

[30] These theoretical analyses point to the need for care in applying the "double-fractionation argument" (Belasco, J. G.; Albery, W. J.; Knowles, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2475) to unimolecular reactions of these ether molecular ions. According to this argument, the $^{16}O/^{18}O$ isotope effect should theoretically fall on replacing H by D in the case of a stepwise reaction but remain the same in the case of a synchronous reaction. In contrast to the enzyme reactions for which double-fractionation has been demonstrated, unimolecular reactions of isolated ions may not occur "at a temperature" as such. With a stepwise enzyme reaction, the intermediate can be assumed to be at the temperature of the system, provided the intermediate's lifetime is long enough. With an isolated reaction, the internal energy of an intermediate in a stepwise process is dependent upon, but generally not the same as, the internal energy of the reactant. In the particular case of the ether molecular ions, the small fall in the $^{16}O/^{18}O$ isotope effect predicted for both the stepwise and the concerted model on replacing H by D is in both cases largely an internal energy effect.

sonable to suppose that either the distonic ion is not formed from the molecular ion (at least in this sort of time frame) or the distonic ion once formed decomposes rapidly.

Turning to the isotope effects in the diether, the $^{16}O/^{18}O$ effects are normal (i.e. $>1$) and their magnitudes can be explained more or less satisfactorily using either the concerted or the stepwise mechanism. As modeled, both the concerted and the stepwise mechanisms predict that the $^{16}O/^{18}O$ isotope effect in the $H_{10}$ molecule (IV) should be a little greater than that in the $D_{10}$ molecular (V), thereby matching the experimental results. When we use the stepwise mechanism and stay within the limits mentioned for the energetics, the calculated $^{16}O/^{18}O$ isotope effects can be raised, but the fit to the H/D isotope effects is worsened as a result of the back-reaction from distonic ion to molecular ion becoming more important. In modeling a stepwise mechanism, the energy barrier to the second step can be kept low so that the second step is sufficiently fast to exclude back-reaction. Under these conditions, the predicted $^{16}O/^{18}O$ isotope effect tends to become inverse[26] due to what is sometimes called the "statistical weight effect".[31] Lowering the energy barrier to the second step means that the excess energy is high for this step, and, as a result, the calculated isotope effect depends more strongly on densities of states than on small differences in critical energies.

In the stepwise mechanism, the back-reaction grows in importance as the relative rate of the second step is cut back. In a deuterium-labeled species such as II or III, there will be an isotope effect on this back-reaction, with H transfer being more rapid than D transfer. The overall consequence of this isotope effect on the back-reaction is, in the case of II for example, to reduce somewhat the extent to which loss of $C_2H_4O$ exceeds loss of $C_2H_3DO$. The isotope effect on the back-reaction is greater in the case of III, where $C_2D_4O$ and $C_2H_4O$ loss compete, than in the case of II, *given the model described here* in which replacing the methyl hydrogen atoms by D atoms tends to reduce marginally rate constants for the hydrogen transfer step. Consequently, the ratio $[C_2H_4O\ \text{loss}]/[C_2H_3DO\ \text{loss}]$ with II is predicted to exceed the ratio $[C_2H_4O\ \text{loss}]/[C_2D_4O\ \text{loss}]$ with III in the case of the stepwise mechanism. The opposite is predicted in the case of the concerted mechanism, because here there is no back-reaction and the reduction of the rate of hydrogen transfer due to replacement of the methyl H atoms by D atoms causes $[M - C_2H_4O]^{\bullet+}/[M - C_2D_4O]^{\bullet+}$ from III to exceed $[M - C_2H_4O]^{\bullet+}/[M - C_2H_3DO]^{\bullet+}$ from II.

## Conclusion

The loss of acetaldehyde from benzyl ethyl ether molecular ions is distinguished from the, in some ways, analogous reaction in for example ketone molecular ions by the absence of hydrogen scrambling in the microsecond time frame. The suggestion[4] has been made that hydrogen scrambling does occur in these ether molecular ions but that it is unusually slow, being manifested only at times approaching 100 μs. It has been suggested that this hydrogen scrambling involves the distonic ion intermediate located in a deep well. We have not been able to observe scrambling at the long times. We conclude that the benzyl ethyl ether ion, and the diether ion, remain distinguished from ketone and other molecular ions with regard to hydrogen scrambling.

The stepwise mechanism with twin energy barriers of comparable heights and a deep intermediate well leads to the prediction that hydrogen scrambling should occur not only in the microsecond time frame but also at times as short as nanoseconds. The stepwise mechanism, as modeled here, leads to the prediction that the H/D isotope effect should be lower in the $D_5$ compound (III) than in the $D_2$ compound (II). The concerted mechanism, as modeled here, leads to the prediction that the H/D isotope effect should be greater in the $D_5$ compound, which is what has been found experimentally. The concerted mechanism leads to predicted $^{16}O/^{18}O$ isotope effects, which are in satisfactory agreement with the experimental results. Our conclusion is that loss of acetaldehyde from the $\alpha,\alpha'$-diethoxy-*p*-xylene molecular ion is a concerted, synchronous reaction. The concertedness of this reaction may be a consequence of aromaticity of the reactant and facilitation of hydrogen addition by simultaneous development of the exo double bond.

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# Carbon Acidities of Aromatic Compounds

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**Abstract:** We report experimental intrinsic carbon acidities and theoretical AM1 results on benzene derivatives and nitrogen heterocyclics. When benzene and pyridine are compared, in-ring aza substitution increases the acidity, i.e. decreases the acid dissociation energy ($\Delta H°_{\text{acid}}$) by 9.7 kcal/mol. Further aza substitution in 1,2- and 1,3-diazine increases the acidity by an additional 8.6 and 5.8 kcal/mol, respectively. However, in 1,4-diazine, where the deprotonated carbon must be adjacent to nitrogen, lone-pair repulsion decreases the acidity below pyridine. The in-ring aza-substitution effects are qualitatively similar to those observed in azoles by Taft et al., but their parameters for lone-pair repulsion and electronegative substituents do not reproduce the effects quantitatively. The electron-withdrawing substituents F, $CF_3$, CN, and $NO_2$ also increase the acidity of benzene by 13.5, 13.6, 17.5, and 46.5 kcal/mol, and $CHCH_2$ increases it by 9.7 kcal/mol. The effects of F and $CHCH_2$ demonstrate that the ring acidity is affected by the $\sigma$ rather than $\pi$ donating or withdrawing ability of substituents. Ab initio calculations at the MP2=FC/6-31G*//RHF/6-31G level were performed on pyridine and diazines. The computed ab initio DPEs were consistently higher than the experimental values by about 22 kcal/mol. Semiempirical computations using Dewar's AM1 method for 1,4-diazine suggest that a correction of 11 kcal/mol is needed for adjacent lone-pair repulsion. With this correction, AM1 predicts qualitatively sensible deprotonation sites for diazines and F-, CN-, $CF_3$-, and $CHCH_2$-substituted benzenes and reproduces the deprotonation energies within 6 kcal/mol.

The intrinsic gas-phase acidities of organic compounds reflect structural effects on the stabilities of the conjugate anions in the absence of complicating solvent effects. Also, many organic anions can be generated readily in the gas phase but in solution only under extreme conditions. These facts allowed the measurement of the gas-phase acid dissociation energies $\Delta H°_{\text{acid}} = \Delta H°_{\text{D}}(A^- - H^+)$ of many carbon acids such as acetylene, aldehydes and ketones, cyclopentadiene derivatives, and substituted toluenes.[1,2] Some