



The Bowie group has synthesized gas-phase carbon clusters involved in interstellar chemistry, uncovering novel rearrangements as shown for C₄. The background comes courtesy of the Hubble Telescope.

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Guest Editorial

John Hamilton Bowie: An Appreciation

Richard A. J. O'Hair

Aust. J. Chem. **2003**, *56*, 343–348.



Students, collaborators, colleagues, and friends of John Bowie gratefully acknowledge his diverse and important contributions to organic chemistry and celebrate his sixty-fifth birthday.

Reviews

Magnetic Resonance Studies of β -Amyloid Peptides

*Tong-Lay Lau, Kevin J. Barnham,
Cyril C. Curtain, Colin L. Masters,
Frances Separovic*

Aust. J. Chem. **2003**, *56*, 349–356.

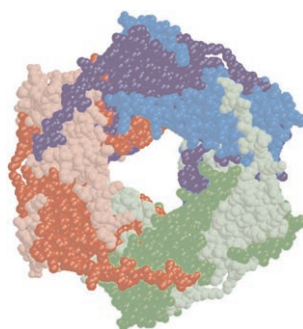


The β -amyloid peptide A β (1–28) plays a central role in Alzheimer's disease and undergoes a structural transition to form aggregates of amyloid fibrils in the brain. In ongoing efforts to determine the relationship between neurotoxicity and conformational changes, this paper reviews the structural investigations of A β and A β fragments which, from the apparently contradictory results, illustrate the importance of studying the full-length peptide.

Intracellular Protein Unfolding and Aggregation: The Role of Small Heat-Shock Chaperone Proteins

*Teresa M. Treweek, Amie M. Morris,
John A. Carver*

Aust. J. Chem. **2003**, *56*, 357–367.



Small heat shock proteins (sHsps) are a family of molecular chaperones that limit unwanted protein self-interaction. Such aggregates are associated with a variety of diseases including cataract and Alzheimer's diseases. The structural and mechanistic aspects of sHsps are reviewed with respect to their ability to act as highly efficient chaperones.

Full Papers

Discrimination Effects in MALDI-MS of Mixtures of Peptides—Analysis of the Proteome

*William I. Burkitt, Anastassios
E. Giannakopoulos, Foteini Sideridou,
Sajid Bashir, Peter J. Derrick*

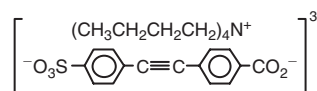
Aust. J. Chem. **2003**, *56*, 369–377.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) has become an analytical method of choice for the determination and characterization of proteins and peptides in the context of proteomics. The phenomenon of peptide ion suppression can reduce the usefulness of this technique, and hence an understanding of why this happens, and how to limit it, is important.

Structural Effects on the Gas Phase Reactivity of Organic Salt Complexes: Substitution versus Hofmann Elimination

Scott Gronert, Lil-Myra Fong

Aust. J. Chem. **2003**, 56, 379–383.

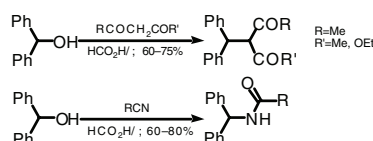


Mass spectrometry offers a means of studying organic salt complexes in the gas phase. Tetraalkylammonium–dianion complexes undergo substitution and elimination reactions. Collision-activated dissociation (CAD) studies were used to study their reactivity and linked with ab initio calculations on a model complex. Selectivity in the gas-phase reactions provides information on the reactivity and insights into condensed-phase reaction mechanisms.

Reactions of Active Methylene Compounds with Benzhydrol During Solvolysis in Formic Acid

Glen C. Gullickson, David E. Lewis

Aust. J. Chem. **2003**, 56, 385–388.

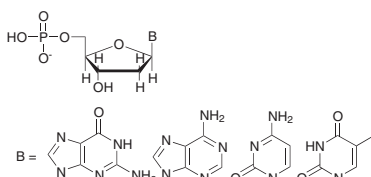


β -Dicarbonyl compounds containing substantial enol at equilibrium react with benzhydrol in refluxing formic acid to give C-alkylation products. Cyano compounds with little equilibrium enol give N-benzhydrylamides by the Ritter reaction. The reaction conditions require neither halogenated reaction solvents nor chromatography.

Gas Phase Reactions of Trimethylborate with the $[M - H]^-$ Ions of Nucleotides and Their Non-covalent Homo- and Heterodimer Complexes

Ana K. Vrkic, Richard A. J. O'Hair

Aust. J. Chem. **2003**, 56, 389–399.



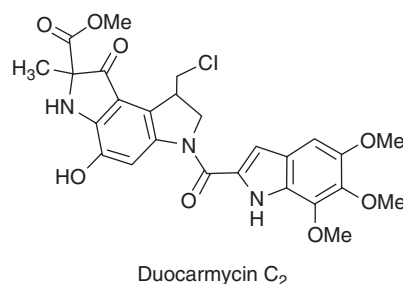
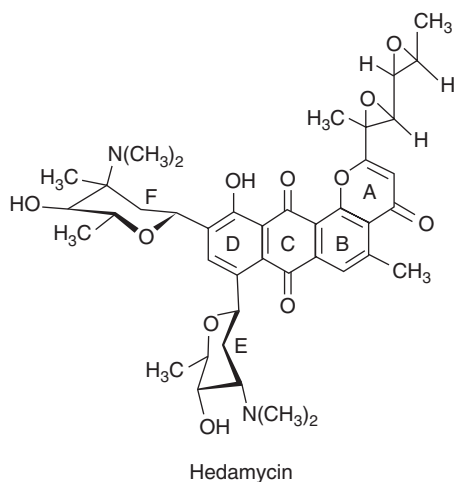
The gas-phase chemistry of deprotonated monomers and dimers of nucleotides (see graphic) have been examined in a quadrupole ion trap. Under collision-induced dissociation conditions, the monomers fragment via base loss whereas the dimers form monomers. Ion–molecule reactions with trimethylborate yield adducts which spontaneously lose between one and three methanol molecules.

Rapid Determination of Sequence Selectivity and Stability of Alkylated Oligonucleotide Adducts by Electrospray Tandem Mass Spectrometry

Michelle L. Colgrave, Paula Iannitti-Tito, Geoffrey Wickham, Margaret M. Sheil

Aust. J. Chem. **2003**, 56, 401–413.

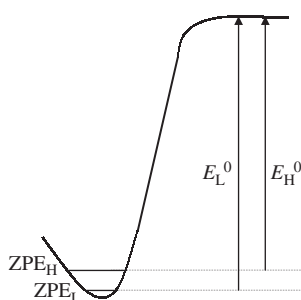
ESI-MS/MS to pre-screen ligand–oligonucleotide complexes prior to performing more detailed structural studies is demonstrated. The binding of four antitumor antibiotics (the structures of two are shown) to a number of self-complementary oligonucleotides was studied by means of the title technique. Subtle selectivity differences were not evident from conventional sequencing studies on larger segments of DNA.



Kinetic Isotope and Collision Energy Effects in the Dissociation of Chloride and Bromide Adducts of Aliphatic Alcohols, Benzaldehyde, and 2,4-Pentanedione

Rodinei Augusti, Xubin Zheng,
M. Turowski, R. Graham Cooks

Aust. J. Chem. **2003**, 56, 415–421.

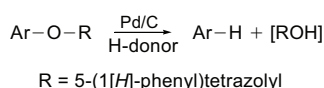


Lower collision energies and multiple collision conditions favoured larger kinetic isotopic effects in the title adducts, an expected feature of easily dissociated cluster ions. These results were correctly predicted by ab initio Hartree–Fock and DFT methods with large basis sets. Interestingly, the intermolecular KIEs in this study tend to be normal, while intramolecular isotope effects in halides, notably of the type $M_1Cl^+M_2$ are inverse, as a consequence of the lower zero-point energies associated with the heavier isotopomers.

Metal-Assisted Reactions. Part XXX. Control of Rates of Heterogeneously Catalyzed Transfer Hydrogenolysis through Changes in Solvent Composition

José A. C. Alves, Amadeu F. Brigas,
Robert A. W. Johnstone

Aust. J. Chem. **2003**, 56, 423–428.

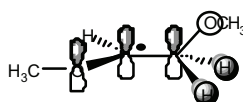


Gas-phase heterogeneous catalysis is widely studied, being of economic importance to large-scale chemistry; liquid-phase heterogeneous catalysis has not been as widely explored. Here the relation of adsorption isotherms to solvent and concentration effects on the rate of the reaction shown have been investigated. The rate of catalysis was changed from zero to a maximum and back to zero by varying the solvent system.

Homoanomeric Effect in the 1,2-Dimethoxyethyl Radical

David J. Henry, Athelstan L. J. Beckwith,
Leo Radom

Aust. J. Chem. **2003**, 56, 429–436.

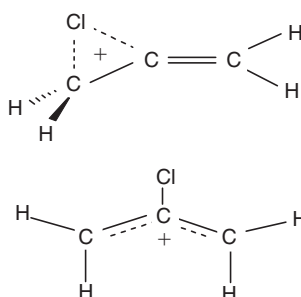


A homo-anomeric effect is found to stabilize the 1,2-dimethoxyethyl radical ($\text{CH}_3\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2\text{OCH}_3$) in a conformation in which the singly occupied orbital at the radical centre is approximately coplanar with the p-type lone pair on oxygen and with the $\beta\text{-C-O}$ bond.

An Investigation of Gaseous α -Halogenated Carbocations and Isomeric Halonium, Halenium, and Allylhalonium Ions

Robert W. Holman, Jennifer Davis,
Amy Walstrom, Michelle McCombs,
Gina Jackson, Shannon Sullivan,
Michael L. Gross

Aust. J. Chem. **2003**, 56, 437–441.



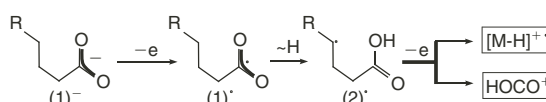
The mass spectrometer is a means of studying gas-phase reactions in which factors such as solvent effects are eliminated. This article addresses the nature and extent of the stabilization of alkyl, vinyl, and 2-allyl carbocations from halogen participation by neighbouring halogen atoms. It is postulated that a bridged species involving the halogen atom is formed.

Unimolecular Rearrangements of Transient Carboxy Radicals and Cations

Detlef Schröder, Héloïse Soldi-Lose,
Helmut Schwarz

Aust. J. Chem. **2003**, 56, 443–451.

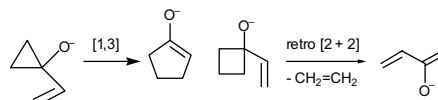
Charge reversal and neutralization–reionization are important mass spectrometric techniques for the characterization of gaseous ions. Using these techniques, a detailed study on the some aliphatic carboxylate ions, RCOO^- , reveals that for the neutral radicals, a novel hydrogen rearrangement, as shown, is a possibility.



Unimolecular Rearrangements and Fragmentations in the Gas Phase: [1,3] Sigmatropic Isomerizations and [2 + 2] Cycloreversions

Mohammad R. Ahmad, Steven R. Kass

Aust. J. Chem. **2003**, 56, 453–458.

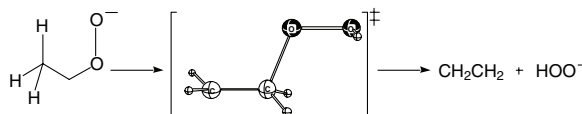


Several alkoxides were generated at a variety of temperatures ranging from -40 to 300°C . When strain is present in the substrate (three- and four-membered rings), anion-accelerated [1,3] sigmatropic rearrangements and [2 + 2] cycloreversions take place at modest temperatures ($\leq 75^\circ\text{C}$).

Fragmentations of Deprotonated Alkyl Hydroperoxides (ROO^-) upon Collisional Activation: A Combined Experimental and Computational Study

Stephen J. Blanksby, Shuji Kato,
Veronica M. Bierbaum,
G. Barney Ellison

Aust. J. Chem. **2003**, 56, 459–472.



The collision-induced dissociation mass spectrum of the CH_3COO^- anion is found to give predominantly HO^- fragment anions whilst $\text{CH}_3\text{CH}_2\text{OO}^-$ and $(\text{CH}_3)_3\text{COO}^-$ produce mostly HOO^- . These results can be rationalized in terms of unimolecular rearrangements occurring via initial abstraction of a proton from the α -carbon in the case of CH_3COO^- or the β -carbon for $\text{CH}_3\text{CH}_2\text{OO}^-$ and $(\text{CH}_3)_3\text{COO}^-$.

Unimolecular Gas-Phase Reactions of Diethyl Phthalate, Isophthalate, and Terephthalate upon Electron Ionization

Susumu Tajima, Masashi Mamada,
Satoshi Nakajima, Yutaka Takahashi,
Nico M. M. Nibbering

Aust. J. Chem. **2003**, 56, 473–479.

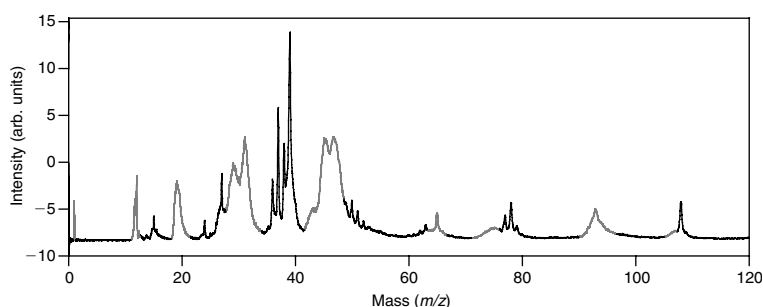
Unimolecular gas-phase reactions of the title compounds were investigated by use of mass-analyzed ion kinetic energy (MIKE) spectrometry and deuterium labelling. The results disagree with an earlier literature proposal, namely that the loss of ethoxy radicals is not the fragmentation pathway. Isophthalate and terephthalate fragment differently still.

Ultraviolet Laser Irradiation of Low Concentration Liquid Microjets: Solute Evaporation and Solvent Initiated Reactivity

Wendy L. Holstein, Laura M. Dobeck,
Dale E. Otten, Gregory F. Metha,
Mark A. Buntine

Aust. J. Chem. **2003**, 56, 481–487.

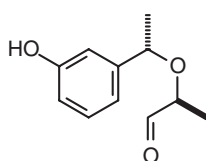
The UV laser-induced ion formation in liquid beams is a useful as a tool for investigating ejection mechanisms at or near the liquid surface. Here, the photochemistry of a 10^{-3} M solution of anisole in ethanol has been determined using 266 nm 1 + 1 resonance-enhanced multiphoton ionization in conjunction with a liquid microjet time-of-flight mass spectrometer.



Regioselectivity in the Syntheses of Enantiopure 2-Benzopyrans through Intramolecular Cyclization of Tethered Lactaldehydes. Conformations of the Products

Rachna Aggarwal, Anthony A. Birkbeck,
Robin G. F. Giles, Ivan R. Green,
Yolanta Gruchlik, Francois J. Oosthuizen

Aust. J. Chem. **2003**, 56, 489–498.



The ability to perform reactions regio- and stereoselectively is a major goal of every organic chemist. The authors here describe the regioselective cyclization of an enantiopure *meta*-hydroxybenzyl lactaldehyde (shown) to afford either 2-benzopyran-4,5- or -4,7-diols through ring closure either *ortho* or *para* to the phenolic hydroxy group, respectively. Furthermore, using titanium tetrakisopropoxide, the 4,5-diols were obtained with complete diastereoselectivity.

High-Resolution Electrospray-Ionization Fourier-Transform Ion Cyclotron Resonance and Gas Chromatography–Mass Spectrometry of Macadamia Nut Oil

Ahmad Mokhtari Fard, Athol G. Turner,
Gary D. Willett

Aust. J. Chem. **2003**, 56, 499–508.

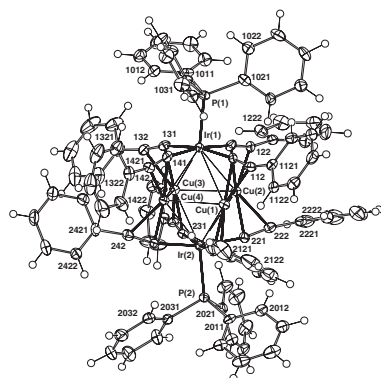


Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) is shown to be a powerful technique for the analysis of fats and oils, in this case using oil from macadamia nuts (shown) as a model. A comparison of the results with other techniques reveals that FTICR-MS provides more detailed information on the composition of the oil, including a relative concentration profile for the free fatty acids present in the oil. The simplicity of the sample preparation is a further advantage of the method.

Crystal and Molecular Structures of Some Alkynyl–Group 9/Group 11 Complexes $[M_2m_4(C_2R)_8(PPh_3)_2]$ ($M = Rh, Ir$; $m = Cu, Ag$; $R = Ph, Fc$ (Ir/Cu only))

Michael I. Bruce, Natasha N. Zaitseva,
Brian W. Skelton, Neil Somers,
Allan H. White

Aust. J. Chem. **2003**, 56, 509–516.



Reports of Pt–Group 11 alkynyl complexes, in which it was observed that the colours varied with the method of isolation and was the result of different degrees of Pt...Pt interactions, has led the authors here to re-examine the crystal and molecular structures of five Group 9/11–phenylethynyl complexes (see the figure for an example). They conclude that there are considerable metal–metal interactions, and that the M_2m_4 cluster formulation is a major contributor to the structure.

Book Review

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