

## Professor Dionis E. Sunko

### A Tribute



Dionis E. Sunko was born in Zagreb, a university center and capital of Croatia, in September 1922. In Zagreb, he had the opportunity to study chemistry at the Technical Faculty of the University of Zagreb, which had a strong Chemistry program in which Vladimir Prelog, later Nobel Prize winner, established a modern organic synthetic laboratory. There, Sunko received the BS degree in chemical engineering in 1946. Subsequently, he pursued research under the supervision of M. Prostenik; he was awarded the PhD degree in 1953 (dissertation title: "Synthesis of Enantiomeric Sphingines").

At that time, synthetic organic chemistry in Zagreb was being pursued both in the University and in chemical industry, particularly in the research laboratories of PLIVA, a pharmaceutical company located in Zagreb. Sunko began his professional career as an engineer by working at PLIVA between 1946-1951, the only period during which he engaged in industrial research. Since 1951, when he obtained a position as Teaching Assistant at the Faculty of Medicine of the University of Zagreb, Sunko has pursued an academic career.

His central scientific interest in physical organic chemistry partially emerged during his postdoctoral fellowship at the University of Illinois, Urbana (1957-1959), where he met a number of leading organic chemists in the field. The intellectual atmosphere in the research group of Robert F. Nystrom, who studied isotope labeling of organic compounds, stimulated Sunko's subsequent scientific work that employed isotope effects to study organic reaction mechanisms. Subsequently, after his return to Croatia, Sunko established the laboratory for physical organic chemistry at the Rudjer Boskovic Institute. There, he initiated collaboration with Stanko Borcic, who also had an abiding interest in the study of organic reaction mechanisms. Together with Borcic, Sunko became a founding father of physical organic

chemistry, not only in Croatia, but also throughout Central Europe. The first physical organic publications to emanate from the Borcic-Sunko collaboration reported their results of painstaking studies of kinetic secondary deuterium effects in the solvolysis of cyclopropylcarbinyl systems. These studies subsequently were extended to include norbornyl and cholesteryl systems, initially in collaboration with Borcic and later with his PhD students Marija Nikoletic, Zdenko Majerski, and Kresimir Humski. Fundamental results published in a series of papers about deuterium isotope effects were incorporated into a review that appeared in an ACS Monograph in 1970. Mention also should be made of an important collaboration between Sunko and V. J. Shiner (Indiana University), which was initiated in 1963 and that later, became formalized through jointly-funded NSF and NIH projects.

At the same time, Sunko served as Assistant Professor and later as an Associate Professor with the Faculty of Technology, University of Zagreb. In 1971, Sunko obtained a permanent position as Full Professor of Chemistry with the Faculty of Science, from which he retired 1992. As a head of the Laboratory of organic chemistry and biochemistry, Sunko continued to work in physical organic chemistry, especially in studies of cyclopropylcarbinyl, cyclobutyl, adamantyl and 7-norbornyl carbocations. His contributions led to improved understanding of hyperconjugation phenomena and the structures of nonclassical carbocations. This focus of this research developed from the use of indirect experimental methods (e.g., kinetic studies and product analyses) to the study of the reactive intermediates in super acids in the solid state, the area in which we have established a especially fruitful collaboration with Sunko.

Sunko's interests have always been in the forefront of the physical organic chemistry. He cherished his worldwide contacts and scientific interactions with the leading researchers in the field. His international activities span a broad spectrum, including invited lectureships (Gordon Conference, Reaction mechanism Symposium, Kimbrough International Symposium, ESOC, ESOR, WISOR), and Visiting Professor appointments at UCLA, USC, Indiana University, University of Southern Illinois, William & Mary College, and Clarkson University.

As a professor at the faculty of Science of the University of Zagreb, Sunko has always played a full and active role. He developed new teaching methods in fundamental organic chemistry and established university courses in physical organic chemistry on the undergraduate and graduate levels. In 1997, Sunko was awarded Professor Emeritus status at the University of Zagreb, and he was elected as a full member of the Croatian Academy of Science and Arts. He remains very active to this day; he visits the Chemistry Department daily, attends seminars, group colloquia, and organizes meetings. His experience continues to inspire students and colleagues in the Department of Chemistry, Faculty of Science, and throughout the academic community.

Hrvoj Vancik  
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### **Curriculum vitae**

Place and Date of Birth: Zagreb, Croatia, September 26, 1922

Marital Status: married to Lia Raffaelli, two sons (Denis 1959, Aleksandar 1960)

**Address**

**Office:** University of Zagreb, Faculty of Science  
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**Education**

1946 University of Zagreb, Dipl. Ing. Degree in Chemistry  
1953 University of Zagreb, Ph. D. in Chemistry  
1957-59 University of Illinois, Urbana, IL, USA (postdoc.)

**Professional Positions**

1945-51 Chemist, Research and Development Division, "Pliva" Chemical Works  
1951-59 Research assistant, Medical Faculty, University of Zagreb  
1959-74 Research associate to scientific advisor, head  
Laboratory of physical-organic chemistry, Institute Ruder Boskovic, Zagreb  
1963-65 Chairman, department of Organic chemistry and Biochemistry  
1969-72 Institute Ruder Boskovic  
1959-65 Assistant professor to associate professor, Faculty of Technology,  
U. of Zagreb  
1971-92 Full profesor, head, Laboratory of organic chemistry and Biochemistry  
Faculty of Science, U. of Zagreb  
1992 Retired  
1997 Professor emeritus U. of Zagreb

**Visiting Professorships**

1966 University of California, Los Angeles, CA  
1967 University of Southern California, Los Angeles, CA  
1973 Indiana University, Bloomington, IN  
1977 University of Southern Illinois, Carbondale, IL  
1978/79 College of William & Mary, Williamsburg, VA  
1983 Indiana University, Bloomington, IN  
1987 Clarkson University, Potsdam, NY

**Honors and Awards**

1967 Rudjer Boskovic award for scientific achievement (jointly with S. Borcic)  
1992 Republic of Croatia award for lifetime achievement  
1999 "Bozo Tezak" medal of the Croatian Chemical Society  
1998- Fellow of the Croatian Academy of Science and Arts

**Publications and lectures**

More than 100 scientific papers published in professional journals. Invited speaker at scientific congresses and other universities. Speaker at scientific meetings and universities at home and abroad.

**Research Interests**

Synthetic and physical organic chemistry; reaction mechanisms, isotope effects in solvolytic reactions, structure and reactivity of carbocations.

**Memberships in Professional Societies and Committees**

- 1946- Member, Croatian Chemical Society  
1957-66 Member of the Editorial Board of *Croatica Chemica Acta*  
1968-70 President Croatian Chemical Society  
1974-78 President, Union of Yugoslav Chemical Societies  
1966- Member, American Chemical Society  
1982- Fellow, Royal Society of Chemistry, London  
1988-92 President, Croatian Society of Natural Sciences  
1990-97 Member editorial board, *Journal of Physical Organic Chemistry*  
1991-92 Member, Republic of Croatia Council for Education  
1992- Member, International Advisory Board, *Perkin Transactions 2*  
1979-93 Member, International board of European Symposia on Organic Chemistry (ESOC)  
1991- Member, International Advisory Committee, European Symposia on Organic Reactivity (ESOR).  
1992-97 Corresponding member of the Croatian Academy of Science and Arts (HAZU)  
1992-97 Member. Organizing Committee of the Winter School on Organic Reactivity (WISOR)  
1997- Fellow of the Croatian Academy of Science and Arts

**Invited Lectures**

Gordon Research Conferences, Reaction Mechanism Symposium, Kimbrough International Symposium, ESOC, ESOR, WISOR, Harvard, Yale, UCLA, USC, UCI, U. of Ill, Cornell, Rochester, Minnesota, Wisconsin, Princeton, Kent, York, Mainz, Heidelberg, Erlangen, ETH, Padova, Moskva.

1991 Regional coordinator and member of the scientific committee (WISOR) u Bressanone, Italy

**Important Publications****a) Reviews and Monographs:**

1. Infrared Spectroscopy of Long-lived Carbocations in Cryogenic  $\text{SbF}_5$  Matrices.
2. Sunko, D. E. In *Stable Carbocation Chemistry*; Prakash, O. K.; Schleyer, P. v. R., Eds; Wiley & Sons: New York, 1997; pp 349-388.
3. Secondary Deuterium Isotope Effects on Reactions Proceeding Through Carbocations.
4. Sunko, D. E.; Hehre, W. J. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; John Wiley & Sons, Inc.: New York, 1983; Vol.14, pp 205-246.
5. Secondary Deuterium Isotope Effects and Neighboring Group Participation.

6. Sunko, D. E.; Borcic, S. In ACS Monograph 167 *Isotope Effects in Chemical Reactions*; Collins, C. J.; Bowman, N. S., Eds.; Van Nostrand Reinhold Company: New York, 1970; pp 160-212.
7. 4. Interactions in Carbocations and Huckel's  $4n+2$  Rule. Sunko, D. E. *Croat. Chem. Acta* **1980**, *53*, 525.

**b) Original papers:**

1. Experimental and Theoretical Infrared Spectra of the 2-Norbornyl Cation. Koch, W.; Liu, B.; De Frees, D. J.; Sunko, D. E.; Vancik, H. *Angew. Chem., Intl. Ed.* **1990**, *29*, 183.
2. Solid State Chemistry in Antimony Pentafluoride Matrices. Infrared Spectra of Reactive Intermediates. Vancik, H.; Sunko, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 3742.
3. Hyperconjugation and the Angular Dependence of  $\beta$ -Deuterium Isotope Effects.
4. Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 5000.
5. Thermodynamic and Kinetic Secondary Isotope Effects in Cope Rearrangement.
6. Humski, K.; Malojcic, R.; Borcic, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1970**, *92*, 6534.
7. Secondary Deuterium Kinetic Isotope Effects in Acetolysis of 2-Norbornyl-6-d Brosylates.
8. Jerkunica, J. M.; Borcic, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1967**, *89*, 1732.
9. Nature of the Intermediates in the SN1 Type Reactions of Cyclopropylmethyl Derivatives: Solvolysis of Deuterated Cyclopropylmethylbenzene Sulphonates.
10. Borcic, S.; Nikoletic, M.; Sunko, D. E. *Chem. & Ind.* **1960**, 527.

**Complete List of Publications**

1. Über-Benzoyl-acetessigsäure. ( $\beta,\delta$ -Dioxo- $\delta$ -phenylvaleriansäure). Balenovic, K.; Sunko, D. E. *Monatsh. f. Chem.* **1948**, *79*, 1.
2. A Synthesis of  $\alpha$ -Phthalimidopropionaldehyde. Jambresic, I.; Sunko, D. *Arhiv Kem.* **1951**, *23*, 195.
3. Note on the Preparation of Margaric Acid. Sunko D.; Alaupovic, P. *Arhiv Kem.* **1953**, *25*, 259.
4. Studies in the Sphingolipids Series. II. Synthesis of Enantiomeric Sphingines. Sunko, D.E.; Prostenik, M. *J. Org. Chem.* **1953**, *18*, 1532.
5. Studies in the Sphingolipids Series. III. Preparation of Sphingine by the Catalytic Reduction of Tribenzoyl-sphingosine. Munk-Weinert, M.; Sunko D. E.; Prostenik, M. *J. Org. Chem.* **1954**, *19*, 378.
6. On the Reaction of  $\alpha$ -Phthalimidoacid Chlorides with Substituted Sodiomalones. A Method for the Preparation of  $\alpha$ -Amino Ketones and Related Compounds. Sunko, D. E.; Prostenik, M. *Arhiv Kem.* **1954**, *26*, 7.
7. A Synthesis of DL- $\alpha$ -Amino- $\beta$ -hydroxy-valeric Acid (Hydroxynorvaline). Sunko, D. E.; Kistic, A. *Arhiv Kem.* **1955**, *27*, 31.
8. 2-Hexadecyonic Acid. Sunko, D. E.; Vujanovic, N. *Arhiv Kem.* **1955**, *27*, 217.
9. The Reduction of Some Phthalamic Acids with Lithium Aluminum Hydride. Sunko, D. E. *Arhivkem.* **1955**, *27*, 183.

10. Studies in the Sphingolipids Series. IV. Determination of Configuration of the Amino Carbon Atom in Sphingosine. Prostenik, M.; Munk-Weinert, M.; Sunko, D. E. *J. Org. Chem.* **1956**, *21*, 406.
11. Synthesis of DL-2-Mercaptohistidine- $\alpha$ -C14 and DL-Ergothioneine- $\alpha$ -C14. Sunko, D.E.; Wolf, G. *J. Am. Chem. Soc.* **1958**, *80*, 4405.
12. Reaction of Unsaturated Organic Compounds with Tritium Gas. Nystrom, R. F.; Sunko, D. E. *Atomlight* **1959**, *Jan.*
13. Nature of the Intermediates in the SN1 Type Reactions of Cyclopropylmethyl Derivatives: Solvolysis of Deuterated Cyclopropylmethylbenzene Sulphonates. Borcic, S.; Nikoletic, M.; Sunko, D. E. *Chem. & Ind.* **1960**, 527.
14. Secondary Hydrogen Isotope Effects. III. Acetolysis of endo- and exo-Norbornyl-5,6-d2 p-Bromobenzenesulfonates. Borcic, S.; Belanic-Lipovac, V.; Sunko, D. E. *Croat. Chem. Acta* **1961**, *33*, 35.
15. The Non-Equivalency of Methylene Ring Carbon Atoms in the Solvolysis of Cyclopropylmethyl Derivatives. Borcic, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1961**, *83*, 2777.
16. Secondary Hydrogen Isotope Effects. V. Internal Rearrangement in the Acetolysis of Deuterium Labeled Cyclopropylmethyl Benzenesulfonates. Borcic, S.; Sunko, D. E. *Croat. Chem. Acta* **1961**, *33*, 77.
17. Metabolism Studies with DL-[ $\alpha$ -C14] Ergothioneine. Wolf, G.; Bergan, J. G.; Sunko, D. E. *Biochim. Biophys. Acta* **1961**, *54*, 287.
18. Secondary Hydrogen Isotopes Effects. IV. Solvolysis Rates of Specifically Deuterium Labeled Cyclopropylmethyl Benzenesulfonates. Borcic, S.; Nikoletic, M.; Sunko, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 1615.
19. Tritium Distribution in 4-Octene Prepared by Catalytic Hydrogenation. Borcic, S.; Strelkov T.; Sunko, D. E. *Croat. Chem. Acta* **1962**, *34*, 243.
20. Reactions of Cyclopropylmethyl Benzenesulfonate. Energies and Entropies of Activation. Borcic, S.; Humski, K.; Sunko, D. E. *Croat. Chem. Acta* **1962**, *34*, 249.
21. Rate of Tritium Exchange in Diethyl Methyl-d3-malonate-t and Diethyl Malonate-d-t in buffered Aqueous Solutions. Gjurovic-Deletis, O.; Borcic, S.; Sunko, D. E. *Pure & Appl. Chem.* **1964**, *8*, 405.
22. The Effects of Deuterium Substitution on the Solvolysis Rates of (Methylcyclo-propyl)-carbinyl Derivatives. Nikoletic, M.; Borcic, S.; Sunko, D. E. *Pure & Appl. Chem.* **1964**, *8*, 441.
23. Secondary Deuterium Isotope Effects in Solvolyses of Small-Ring Compounds. Nikoletic, M.; Borcic, S.; Sunko, D. E. *Proc. Natl. Acad. Sci. (U.S.)* **1964**, *52*, 893.
24. 1,3-Hydrogen Migration in the Solvolysis of 2-(d3-Cyclopentenyl)ethyl p-Toluenesulfonate. Humski, K.; Borcic, S.; Sunko, D.E. *Croat. Chem. Acta* **1965**, *37*, 3.
25. Secondary Hydrogen Isotope Effects. VII. Ethanolysis Rates of 1,1-Dimethylallyl-3,3-d2 Chloride and 3,3-Dimethylallyl-1,1-d2 Chloride. Belanic-Lipovac, V.; Borcic, S.; Sunko, D. E. *Croat. Chem. Acta* **1965**, *37*, 61.
26. Secondary Hydrogen Isotope Effects. VIII. Rate of Formation of Diethyl Malonate Anions. Servis, K.L.; Gjurovic-Deletis, O.; Borcic, S.; Sunko, D. E. *Croat. Chem. Acta* **1965**, *37*, 191.

27. Base Catalyzed Deuteration of Norcamphor and Dehydronorcamphor. Jerkunica, J. J.; Borcic, S.; Sunko, D. E. *Tetrahedron Lett.* **1965**, 4465.
28. Deuterium Scrambling During Stereochemical Equilibration of endo- and exo-Norbornanol-3,3-d<sub>3</sub>. Humski, K.; Borcic, S.; Sunko, D.E. *Croat. Chem. Acta* **1966**, 38, 55.
29. Secondary Hydrogen Isotope Effects. IX. Solvolysis Rates of Methyl and Methyl-d<sub>3</sub> Substituted Cyclopropylcarbinyl and Cyclobutyl Derivatives. Nikoletic, M.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1967**, 23, 649.
30. "The Bicyclobutonium Ion". Reaction of (1-Methycyclopropyl)-carbinyl and 1-Methylcyclobutyl Methanesulfonates with Sodium Borohydride under Solvolytic Conditions. Majerski, Z.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1967**, 23, 661.
31. Oxygen Bonding in Haemoglobin. Maricic, S.; Leigh, J. S., Jr.; Sunko, D. E. *Nature* **1967**, 214, 462.
32. Secondary Deuterium Kinetic Isotope Effects in Acetolysis of 2-Norbornyl-6-d Brosylates. Jerkunica, J. M.; Borcic, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1967**, 89, 1732.
33. s-Participation and Secondary Deuterium Isotope Effects: the Norbornyl Case. Jerkunica, J. M.; Borcic, S.; Sunko, D.E. *Chem. Commun.* **1967**, 1302.
34. Methyl-d<sub>3</sub> Isotope Effects and the Origin of  $\alpha$ -Methyl Substituent Effects. Servis, K. L.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1968**, 24, 1247.
35. The Magnitude of Secondary  $\beta$ -Deuterium Isotope Effects in Cases of  $\pi$ -Participation. Jerkunica, J.M.; Borcic, S.; Sunko, D.E. *Chem. Commun.* **1968**, 1488.
36. n- and  $\pi$ -Participation and Secondary Deuterium Isotope Effects. Eliason, R.; Tomic, M.; Borcic, S.; Sunko, D.E. *Chem. Commun.* **1968**, 1490.
37. Competitive Reactions of Nucleophiles. Solvolyses of Cyclopropylcarbinyl and Cyclobutyl Methanesulfonates in the Presence of NaBH<sub>4</sub>. Majerski, Z.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1969**, 25, 301.
38. Thermodynamic Secondary Deuterium Isotope Effect in the Thermal Rearrangement of Biallyl. Malojcic, R.; Humski, K.; Borcic, S.; Sunko, D. E. *Tetrahedron Lett.* **1969**, 2003
39. Secondary Deuterium Isotope Effects in the Cope Rearrangement. Humski, K.; Strelkov, T.; Borcic, S.; Sunko, D. E. *Chem. Commun.* **1969**, 693.
40. Secondary Deuterium Isotope Effects and Neighboring Group Participation. Sunko, D.E.; Borcic, S. In ACS Monograph 167 *Isotope Effects in Chemical Reactions*; Collins, C. J.; Bowman, N. S., Eds; Van Nostrand Reinhold Company: New York, 1970.
41. Label Scrambling in the Hydrolysis and Borohydride Trapping Products of [1,1-2H<sub>2</sub>]Cyclopropylmethyl, [1-2H<sub>1</sub>]Cyclobutyl and [2,2,4,4-2H<sub>4</sub>]Cyclobutyl Methanesulfonates. Majerski, Z.; Borcic, S.; Sunko, D. E. *Chem. Commun.* **1970**, 1963.
42. Thermodynamic and Kinetic Secondary Isotope Effects in Cope Rearrangement. Humski, K.; Malojcic, R.; Borcic, S.; Sunko, D.E. *J. Am. Chem. Soc.* **1970**, 92, 6534.
43. Competitive Reactions of Nucleophiles - II. Solvolysis of  $\alpha,\alpha$  and  $\gamma,\gamma$ -Dimethylallyl Chlorides. Eckert-Maksic, M.; Majerski, Z.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1971**, 27, 2219.
44. Rates of Oxidation of Some Bicyclic Alcohols with Silver Carbonate on Celite. Eckert-Maksic, M.; Tusek, Lj.; Sunko, D. E. *Croat. Chem. Acta* **1971**, 43, 79.

45. Temperature and Concentration Dependence of the Paramagnetic Induced Shifts in Proton Magnetic Spectroscopy. Tomic, L.; Majerski, Z.; Sunko, D.E. *Chem. Commun.* **1971**, 719.
46. Tris(dipivalomethanato)holmium Induced NMR Shifts. Tomic, L.; Majerski, Z.; Tomic, M.; Sunko, D. E. *Croat. Chem. Acta* **1971**, 43, 267.
47. Competitive Reactions of Nucleophiles - III. The Azide Probe. Kovacevic, D.; Majerski, Z.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1972**, 28, 2469.
48. Solvolysis Rates of 7-Methyl- and 7-Methyl-d<sub>3</sub>-7-norbornyl Tosylates in Trifluoroethanol. A Case of an Apparent Breakdown of the mY Relationship. Sunko, D. E.; Szele, I.; Tomic, M. *Tetrahedron Lett.* **1972**, 1872.
49. Solvolysis in Fluoroalcohols II. Anomalous Behavior of tert-Butyl Chloride and 7-Methyl-7-norbornyl Tosylate in Hexafluoroisopropanol-Water Mixtures Sunko, D. E.; Szele, I. *Tetrahedron Lett.* **1972**, 3617.
50. Secondary Deuterium Isotope Effects in the Solvolysis of Cyclobutyl and Cyclopropylcarbinyl Methanesulfonates. Goricnik, B.; Majerski, Z.; Borcic, S.; Sunko, D. E. *J. Org. Chem.* **1973**, 38,1881.
51. Stereochemistry of the Solvolysis of Menthyl Tosylate. An Example of Retained Chair Conformation in the Transition State. Hirsl-Starcevic, S.; Majerski Z.; Sunko, D. E. *J. Am. Chem. Soc.* **1974**, 96, 3659.
52. The Mechanism of Olefinic Cyclizations. A Case of  $\pi$ -Participation. Polla, E.; Borcic, S.; Sunko, D. E. *Tetrahedron Lett.* **1975**, 799.
53. Methyl-d<sub>3</sub> Isotope Effects,  $\alpha$  -Methyl Hydrogen Rate Effects, and the Analysis of some Solvolytic Reaction Mechanisms. Fisher, R. D.; Seib, R. C.; Shiner, V. J., Jr.; Szele, I.; Tomic, M.; Sunko, D. E. *J. Am. Chem. Soc.* **1975**, 97, 2408.
54. Secondary Deuterium Isotope Effects and the Conformation of Transition States in the Solvolyses of  $3\alpha$  -and  $3\beta$  - Cholestanyl Brosylates. Tarle, M.; Borcic, S.; Sunko, D. E. *J. Org. Chem.* **1975**, 40, 2949.
55. Secondary Deuterium Isotope Effects as Sensitive Probe for Double Bond Participation. The Structure of Cholesteryl Cation. Tarle, M.; Borcic, S.; Sunko, D. E. *J. Org. Chem.* **1975**, 40, 2954.
56. Model Calculations of Secondary Deuterium Isotope Effects in Hydrogen Bridged Carbonium Ions. Wilcox, C. F., Jr.; Szele, I.; Sunko, D. E. *Tetrahedron Lett.* **1975**, 4457.
57. Secondary Deuterium Isotope Effects in the Solvolysis of cis- and trans-2-Acetoxy-cyclohexyl 2,2,2-Trifluoroethanesulfonates. Richter, S.; Bregovec, I.; Sunko, D. E. *J. Org. Chem.* **1976**, 41, 785.
58. Hyperconjugation and the Angular Dependence of  $\beta$  -Deuterium Isotope Effects. Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, 99, 5000.
59.  $\pi$  -Participation in Solvolysis and Secondary Deuterium Isotope Effects. Octahydrodimethanonaphthalene System. Malojcic, R.; Borcic, S.; Sunko, D. E. *Croat. Chem. Acta* **1977**, 49, 743.
60. 5-Methoxyl Participation in Solvolysis and Secondary Deuterium Isotope Effects. Eliason, R.; Borcic, S.; Sunko, D. E. *Croat. Chem. Acta* **1978**, 51, 203.
61. On the Conformational Dependence of Secondary  $\beta$  -Deuterium Isotope Effects. DeFrees, D. J.; Hehre, W. J.; Sunko, D. E. *J. Am. Chem. Soc.* **1979**, 101, 2323.



62. Hyperconjugation and Homohyperconjugation in the 1-Adamantyl Cation. Qualitative Models for  $\beta$ -Deuterium Isotope Effects. Sunko, D.E.; Hirsl-Starcevic, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163.
63. n-Participation and Secondary Deuterium Isotope Effects in Solvolysis of 1-Aryl-4-methoxy-1-butyl Chlorides. Are There Two Distinct  $k_o$  Pathways? Mihel, I.; Sisteck, J.; Borcic, S.; Humski, K.; Sunko, D. E. *J. Org. Chem.* **1979**, *44*, 4091.
64. Secondary Deuterium Isotope Effects in the Solvolysis of 1-Aryl-5-methyl-5-heptenyl Chlorides. Comparison of  $\pi$ - and n-Participation Mechanisms. Polla, E.; Borcic, S.; Sunko, D. E. *J. Org. Chem.* **1979**, *44*, 4096.
65. Hydrogen Participation vs. Elimination. The Role and the Fate of Neighboring Hydrogen in the Solvolysis of Neomenthyl Tosylate. Hirsl-Starcevic, S.; Majerski, Z.; Sunko, D. E. *J. Org. Chem.* **1980**, *45*, 3388.
66. Interactions in Carbocations and Hückel's  $4n+2$  Rule. Sunko, D. E. *Croat. Chem. Acta* **1980**, *53*, 525.
67. On the Nonconcertedness of Allylic Cation Promoted  $\pi$ -Cyclization Reactions. Ladika, M.; Bregovec, I.; Sunko, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 1285.
68. The Role of Theory in Teaching Organic Chemistry. Sunko, D. E. *Pure & Appl. Chem.* **1983**, *55*, 375.
69. Secondary Deuterium Isotope Effects on Reactions Proceeding Through Carbocations. Sunko, D. E.; Hehre, W. J. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; John Wiley & Sons, Inc.: New York, 1983; Vol.14, p. 205.
70. The 7-Norbornyl Cation. Structure and Interactions. Sunko, D.E.; Vancik, H.; Deljac, V.; Milun, M. *J. Am. Chem. Soc.* **1983**, *105*, 5364.
71. Allylic Cations in Solvolysis. A Case of Non-participation. Ladika, M.; Sunko, D. E. *Croat. Chem. Acta* **1984**, *57*, 179.
72. Solvolysis Rate of 3-Methyl-2-(3-pentynyl)-2-cyclohexyl p-Nitrobenzoate. A Model System for  $\pi$ -Participation of the CC Triple Bond. Ladika, M.; Sunko, D. E.; Borcic, S. *Croat. Chem. Acta* **1984**, *57*, 331.
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74. Solvolysis of 2-Alkenyl-2-cyclohexenyl p-Nitrobenzoates. Ladika, M.; Sunko, D. E. *J. Org. Chem.* **1985**, *50*, 4544.
75.  $^1\text{H}$  NMR Study of Hydrogen Bonding in Fluorinated Alcohols with Ethers. Jursic, B.; Ladika, M.; Sunko, D.E. *Tetrahedron Lett.* **1985**, *26*, 5323.
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