

Substituent Effects in Radical Chemistry

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Substituent Effects in Radical Chemistry

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PREFACE

Respectably old radical chemistry which plays a major role in life-processes, both desired (breathing, ...) and non-desired (inflammatory diseases, ageing,...) has been gaining new youth in the past decade.

Modern spectroscopy and other physical methods, recent advances in computational methods as well as impressive and mechanistically well-understood syntheses have led to a number of spectacular developments in the field of radical chemistry. The impact of these achievements will reach far beyond the field of organic chemistry, for example into biology and medicine.

New facts and concepts in this rapidly expanding field deserved discussion among a number of leading experts present at the Workshop both for the information and constructive criticism. This happened during a particular brainstorming session and some of the impressions and reflections exchanged are recorded in the Epilogue.

Indeed the topic chosen seems to be quintessential for the whole radical chemistry : understanding and exploiting (single and multiple) substituent effects on radicals.

We had the honour to organise this Workshop because some years ago, in collaboration with L. Stella, we became involved in radical stabilising effects when both a donor and an acceptor (captor) groups are present on a C-radical. This leads to an enhanced stabilisation which we called the captodative effect and we have endeavoured the first extensive investigation of this effect on carbon centered radicals. Nevertheless such an effect was intimated as early as in 1952 by Dewar, but it was not until about 20 years later when Katritzky provided some first experimental results and called this effect "merostabilisation". Similar effect on nitrogen-centered radicals has been discovered and well documented by Balaban under the name "push-pull" stabilisation. There has not yet been reached a complete agreement as to the extent of such an effect but by now more leading groups are active in this field. Owing to this concern it came to light that even the effect of a single substituent may still be subject to controversy. This explains why the organization of such a meeting was of paramount importance.

Thanks to a generous grant from NATO Scientific Affairs Division such a meeting among almost 50 specialists became possible at

Louvain-la-Neuve (Belgium). The lectures and posters were streamlined on the following topics :

- computations concerning both closed and open-shell species;
- kinetic and thermodynamic phenomena;
- ESR techniques;
- devising radical stabilising scales;
- new radical reactions in synthesis.

Many points have been clarified and those which still manage to escape our full understanding will stimulate the participants and, as we hope, the readers of this book to help to solve them.

H.G. Viehe,
Z. Janousek,
R. Merényi,

Louvain-la-Neuve, 1986.