CARBONIUM IONS

Edited by

GEORGE A. OLAH
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio

PAUL von R. SCHLEYER
Department of Chemistry
Princeton University
Princeton, New Jersey

VOLUME I

General Aspects and Methods of Investigation

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CARBONIUM IONS

VOLUME I

GENERAL ASPECTS AND METHODS OF INVESTIGATION

REACTIVE INTERMEDIATES IN ORGANIC CHEMISTRY

Edited by GEORGE A. OLAH and LESTER FRIEDMAN
Case Western Reserve University

A series of collective volumes and monographs on the chemistry of all the important species of organic reaction intermediates:

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Foreword

The study of carbonium ions has come a long way since the days when an American protagonist cautiously avoided writing positive signs on them. We now have a scale of carbonium ion acidities extending over some 30 powers of ten. Ions once known only by inference as intermediates have had their ultraviolet, infrared, Raman, and nuclear magnetic resonance spectra recorded. Heats of formation and electron affinities of organic cations in the gas phase are known. Ionic reaction mechanisms are now studied with rate measurements, linear free energy relationships, and single, double, and triple isotopic labeling. Synthetic methods are available for ring systems that looked like an alchemist's dream a few years ago. Several available carbonium ions, prodded toward equilibrium, have cascaded into the symmetrical adamantane ring structure, turning a one-time synthetic challenge into a simple preparation. And quantum mechanics now explores the energy of a carbonium ion as a function of its molecular geometry.

These advances in methods are matched by the glimpses of new principles which they have brought. We have symmetrical cations which are also aromatic hydrocarbons; homoaromatic cations write their signatures large on the NMR chart; rate ratios of isomers of up to 15 orders of magnitude tell of charge decalization across space, into π systems, into the bent bonds of cyclopropanes. We know that cations of cyclobutane and bicyclo[*n*.1.1] alkanes are no ordinary carbonium ions, seeming immune to distortions which elsewhere are highly destabilizing.

Yet with all this sophistication, carbonium ion mechanisms are still a field for the explorer. The same "carbonium ion" intermediate, produced in different ways, shows a considerable range of behavior, depending on the different anions, solvent molecules, and reagents in its immediate vicinity. This is a topic in physical organic chemistry, not in the mistaken sense of having made all new results calculable, but because the explorers are working to understand as they discover.

Paul D. Bartlett

Cambridge, Mass.

Editors' Preface

Three years ago we undertook the task of trying to organize a survey of the field of carbonium ion chemistry in the form of an advanced monograph. Although we both have been active in research on carbonium ions, we were not fully aware, at the time the project was begun, of the vast dimensions to which the field had grown, particularly in the past two decades. To cover the entire area a very substantial effort was needed and the cooperation of a large number of colleagues and friends was necessary. We have been very gratified by the favorable response of research workers in the field to our invitations to contribute chapters in their own specialities. As the project proceeded, it became quite obvious that it would be impossible to cover all the material, as originally projected, in fewer than four volumes, if these were to be kept to manageable size.

Thought has been given to the best arrangement of chapters in these volumes. Some authors were able to produce their manuscripts more rapidly than others, and it might have been possible to assemble the volumes from unrelated chapters, in order of receipt. We have felt it better to have each individual volume maintain a coherence and identity by bringing together chapters related in subject matter to one another. Thus, a historical introduction, general aspects, and methods of investigation of carbonium ions are included in this first volume. Major types of such ions will be featured in the second volume, and the third will deal with the classical–nonclassical ion problem. The last volume will contain chapters devoted to diverse types of carbonium ions, and it will have comprehensive subject and author indexes. In addition, each volume will have short indexes.

We have not tried to alter in any way the individual authors' contributions, but, hopefully, we have provided some coordination of topics to minimize overlap and to make a multiauthored book, as much as possible, an organized entity. Consequently, the different chapters reflect their authors' standpoints and philosophy. We felt particularly that exposure of the reader to views from opposing sides of topics in which there is controversy not only would be stimulating, but would further an understanding of the topic. Often, one's opinions and attitudes are influenced by a particularly persuasive argument. It is to the good to have the alternative interpretations available conveniently together, to facilitate comparison. The editors have attempted to survey the fascinating field of carbonium ions impartially by affording the many active workers an opportunity to summarize their viewpoints and evidence. To what extent we have been successful will be decided by the readers.

We should like to express our sincere appreciation not only to the authors whose contributions made this book possible, but also to the numerous colleagues who commented on individual chapters, provided us with additional information (frequently not yet published), and called attention to many aspects of carbonium ions, whose importance we had not fully realized.

As the preparation of a monograph of this size takes a long time, we must apologize to our readers and especially to our co-authors that the unavoidable manuscript collecting and publishing delays have made it impossible to cover the literature to the last minute. In this first volume reference to the literature through 1966 is general, and in frequent instances citations to books published as late as summer, 1967, were added in the galley proof stage.

As the first volume of our monograph is going into production, the second and third volumes are practically complete and in the printer's hands. It is hoped that the whole project will be finished by the end of next year. The cooperation and excellent work of the publisher's staff made the preparation of these volumes a much more pleasant task than we could possibly have anticipated originally.

GEORGE A. OLAH
PAUL V. R. SCHLEYER

January, 1968

Authors of Volume I

E. M. ARNETT, *Department of Chemistry, University of Pittsburgh, and Mellon Institute of Carnegie-Mellon University, Pittsburgh, Pennsylvania*

JOHN D. BALDESCHWIELER, *Department of Chemistry, Stanford University, Stanford, California*

MAURICE M. BURSEY, *Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina*

CLAIR J. COLLINS, *Oak Ridge National Laboratory, Oak Ridge, Tennessee, and University of Tennessee, Knoxville, Tennessee*

J. C. EVANS, *Chemical Physics Research Laboratory, The Dow Chemical Company, Midland, Michigan*

DONALD G. FARNUM, *Department of Chemistry, Michigan State University, East Lansing, Michigan*

GIDEON FRAENKEL, *Department of Chemistry, Ohio State University, Columbus, Ohio*

J. L. FRANKLIN, *Department of Chemistry, Rice University, Houston, Texas*

R. J. GILLESPIE, *Department of Chemistry, McMaster University, Hamilton, Ontario, Canada*

JOHN W. LARSEN, *Department of Chemistry, University of Pittsburgh, and Mellon Institute of Carnegie-Mellon University, Pittsburgh, Pennsylvania*

HARRY P. LEFTIN, *The M. W. Kellogg Co., Piscataway, New Jersey*

NORMAN N. LICHTIN, *Department of Chemistry, Boston University, Boston, Massachusetts*

FRED W. MCLAFFERTY, *Department of Chemistry, Purdue University, Lafayette, Indiana*

COSTIN D. NENITZESCU, *Institute of Organic Chemistry of the Rumanian Academy, Bucharest, Rumania*

GEORGE A. OLAH, *Department of Chemistry, Case Western Reserve University, Cleveland, Ohio*

CHARLES U. PITTMAN, JR., *Department of Chemistry, University of Alabama, University, Alabama*

E. A. ROBINSON, *Department of Chemistry, University of Toronto, Toronto, Ontario, Canada*

MARTYN C. R. SYMONS, *Department of Chemistry, University of Leicester, Leicester, England*

Contents

Volume I. General Aspects and Methods of Investigation

Volume II. Methods of Formation and Major Types

Volume III. Classical and Nonclassical Ions

Volume IV. Miscellaneous Ions. Indexes.

CHAPTER 1

Historical Outlook

COSTIN D. NENITZESCU
Institute of Organic Chemistry of the Rumanian Academy,
Bucharest, Rumania

I. INTRODUCTION

Many scientific theories originate as nothing more than simple schemes or models, invented solely in order to provide an explanation for a particular result. Very often we are satisfied with "the impression that it could not be otherwise." * However, it happens that such a theory might in the long run embrace a much wider field than had initially been foreseen. Thus, as the concept loses its hypothetical character, the point is gradually reached at which it is accepted as the reality itself.

Such an evolution does not take place unless the theory undergoes profound changes. Some statements which originally seemed essential must later be abandoned, while others at first unnoticed or even overlooked prove to be of fundamental importance. We thus see how the atomic

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* E. P. Wigner, Nobel Lecture, 1963.

theory has become an efficient tool in chemistry along with the abandonment of the principle of indivisibility implied by the very word "atom" and the recognition of the importance of the electron shell. Likewise, the theory of electrolytic dissociation acquired a quantitative character when it became obvious that electrolytes, even when ionized in the solid state, never fully dissociate in solution and sometimes dissociate only very slightly. The ions, far from being free, show a complex behavior owing to interactions with ions of opposite charge and with solvent molecules.

Obviously, scientific theories are forever changing their form and content, as they have done in the past and as they will certainly continue to do in the future. The theory of carbonium ions, the history of which we will trace, is no exception to this rule. A book such as the present one aims at faithfully describing some scenes from the middle of a moving picture, the end of which is unknown to the authors. The question arises whether it might be useful to recall the beginning of the story. Many believe it would not. As Aldous Huxley writes*:

> Every generation of scientific men starts where the previous generation left off; and the most advanced discoveries of one age constitute the elementary axioms of the next. We are not in the habit of inspecting the foundation of the houses in which we live. . . . Except for the historians of science, nobody studies at first hand those contributions to knowledge to which the great discoverers of the past owe their scientific reputations.

This is certainly the way in which science advances. History of science does not repeat itself, exactly as political history does not repeat itself. And men who make Science, just as those who make History, must continuously face new situations; the solutions chosen should also be new. But just as the present political situation is the consequence of past events, today's science is the consequence of past thought. From this point of view, the pursuit of the continuous chain of ideas which has led to contemporary science may be, even for the research worker, an attractive and profitable interlude.

It seems convenient to divide the more than 60-year-long history of the existence of carbonium ions into three approximately equal periods differentiated by research themes and methods, each based upon the most advanced discoveries of the preceding epoch.

II. LONG-LIVED CARBONIUM IONS

A. Triarylcarbonium Ions

Less than one year after the discovery of the first stable free radical by Gomberg, in 1900, Norris (263,265) and Kehrmann (214) independently

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* Thomas H. Huxley Memorial Lecture, 1932; A. Huxley, *The Olive Tree*, The Albatross, Leipzig, 1937.

observed that colorless derivatives of triphenylmethane, like triphenylcarbinol and triphenylmethyl chloride, give deep yellow solutions in concentrated sulfuric acid. Triphenylmethyl chloride forms orange complexes with the aluminum and tin chlorides.

It was certainly not by chance that both the first free radical and the first carbonium ion discovered were derivatives of triphenylmethane, but this coincidence was explained only much later. At the time of the original discovery, the intense color of these extraordinary compounds and their sensitivity to hydrolysis were their most remarkable properties. Absorption of light subsequently played an important part in the study of carbonium ions. Many attempts were made to assign quinoid structures to these ions as well as to the triphenylmethyl radical, according to the theories of the time regarding the structure of dyes. We know today that this interpretation was not completely erroneous, although the essential point of the problem was not appreciated.

It was to von Baeyer's credit (13,14) that he recognized the saltlike character of the compounds formed in the solutions of triphenylcarbinol in sulfuric acid and proceeded to suppose a correlation between the formation of salt and the appearance of color—the so-called "halochromy." Previous studies on "the basic properties of oxygen" had shown that certain unsaturated ketones, such as dibenzylidenacetone, formed colored salts with strong acids. In von Baeyer's view the triphenylmethyl radical had the properties of a "composite metal atom" ("zusammengesetztes Metallatom") resembling sodium on the one hand, because it gave a peroxide, and aluminum on the the other hand, because it was capable of forming a hydroxide (triphenylcarbinol), which shows practically no basicity but is still able to form a true salt with sulfuric acid. von Baeyer found that the basicity of triphenylcarbinol is enhanced by the introduction of methoxy groups in the *para* positions of the benzene nuclei. This greater basicity can be recognized by the greater resistance to hydrolysis of the salts. These salts were named *carbonium salts* (13).

The word "carbonium" was apparently used for the first time by Doebereiner in 1816 to designate graphite, considered as a metal because of its opacity, metallic luster, and good conductivity (355). It is difficult nowadays to establish whether von Baeyer was influenced by this old proposal in choosing a name for his salts.

The incongruity of the term "carbonium" was appreciated very early. In 1902 Gomberg (147) wrote: "In my opinion, the name 'carbonium' should be applied to salts in which an increase of the number of valences of the carbon takes place, just as in the case of the ammonium, sulfonium, iodonium, and oxonium salts." For this reason Gomberg proposed the name *carbyl salts*, which, however, never became popular.

Later W. Dilthey and R. Wizinger gave to the compounds of the type $R_3C^+X^-$ the name of carbenium salts (112,113) according to their theory of coordinately unsaturated chromophores (see below). This nomenclature has been maintained in the German literature.

Curiously enough, the perfectly adequate term, *carbocation*, justified by its analogy with *carbanion*, has not found wide acceptance.

Walden (354) and Gomberg (147) used such formulas as $(C_6H_5)_3C^+Cl^-$ or $(C_6H_5)_3C \cdot Cl$ for triphenylmethane in ionizing solvents, while Baeyer preferred the introduction of a special symbol for what he called the "Carboniumvalenz": $(C_6H_5)_3C\sim Cl$ (8).

While von Baeyer's work relied principally upon the classical preparative methods of organic chemistry, Walden (354) in 1902 demonstrated by conductivity measurements the electrolyte character of triphenylmethyl chloride and bromide in sulfur dioxide solution. Since then the use of physical methods has remained a distinctive character of the research in this field. The work of Walden is also remarkable for its utilization of a nonaqueous solvent—liquid sulfur dioxide—possessing an exceptional ionizing power. The importance of the solvents did not in fact escape the attention of earlier workers. Gomberg (147) showed that in some solvents such as benzene and ether, triphenylmethyl chloride is nonionized and colorless, while its solutions in "dissociating solvents," such as SO_2, CH_3COCl, and SO_2Cl_2, are conductors and exhibit a yellow color. Both properties were attributed to the ion $(C_6H_5)_3C^+$. Ionization occurs also when triphenylmethyl chloride is complexed with inorganic halides such as $SnCl_4$, $ZnCl_2$, or $AlCl_3$ (13,147,354):

$$(C_6H_5)_3CCl + SnCl_4 = (C_6H_5)_3C^+ + SnCl_5^-$$

The identity of the colored species of the triphenylmethyl chloride solution in SO_2 and of the triphenylcarbinol solution in sulfuric acid was later confirmed by its very characteristic absorption spectrum (170). The existence of the carbonium salts was finally confirmed preparatively by the independent discoveries of K. A. Hofmann (178) and of Gomberg (149) that triarylcarbinols give with perchloric acid crystalline, colored anhydrous perchlorates, Ar_3CClO_4. From all these facts Hantzsch (170) concluded that the triarylmethyl-type halides can exist in two forms—*pseudo-salts*, Ar_3CCl, containing the halogen directly bound to the central carbon atom, and *true salts*, $[Ar_3C]^+Cl^-$, in which the halogen (or another acid residue) is present as an anion in the secondary sphere of the complex. Hantzsch showed in 1908 (166) and Hammett (163) later confirmed that the molal freezing point depression of the solution of triphenylcarbinol in concentrated sulfuric acid is four times that produced by a nonelectrolyte. This is possible only if a carbonium ion forms in solution:

$$(C_6H_5)_3COH + 2H_2SO_4 \rightleftharpoons (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^-$$

Ionization of the triarylmethyl halides in solution implies the following equilibrium:

$$(C_6H_5)_3CCl \rightleftharpoons (C_6H_5)_3C^+ + Cl^-$$

Ziegler and co-workers (400,402) carried out measurements of conductivity in liquid sulfur dioxide solutions of triphenylcarbonium perchlorates substituted with one, two, or three *p*-methyl or *p*-methoxy groups. As equivalent conductivities of all these compounds differ only slightly, the conclusion was drawn that they are completely ionized electrolytes; conversely, triphenylmethyl halides must be recognized as weak electrolytes.

By an extension of this method, Lichtin and Bartlett (230) and Lichtin and co-workers (231,232) showed that triarylmethyl chloride solutions in SO_2 exist as an equilibrium between molecules, ion pairs, and dissociated ions. In this way total equilibrium constants, K_{exp}, were determined. From these, on the basis of certain premises, the ionization constant, K_1, and the dissociation constant, K_2, could be estimated.

$$Ar_3CCl \overset{K_1}{\rightleftharpoons} Ar_3C^+Cl^- \overset{K_2}{\rightleftharpoons} Ar_3C^+ + Cl^-$$

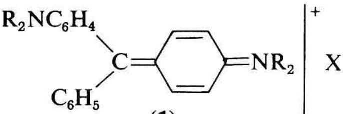
The equilibria between triarylmethyl halides and triarylcarbonium ions have subsequently been detected spectrophotometrically (36,122). The dramatic changes in the visible and UV spectra in passing from covalent molecules to carbonium salts indicate a deep reorganization of the chromophoric system that was difficult to explain initially. A certain confusion was also caused by discrepancies among the results obtained by various physical methods (167,173). Only much later were these problems solved when the difference between ions pairs and free carbonium ions was appreciated. It then became possible, by combining spectrophotometric and conductometric methods, to distinguish ionization from dissociation. Thus, triphenylmethyl chloride ionizes in 0.1, 0.01, and 0.001*M* dry sulfur dioxide solutions to an extent of 3.2, 7.4, and 21%, but only three-fifths of these values represent the degree of dissociation to free ions (295). On the other hand, triphenylcarbinol is essentially completely dissociated in sulfuric acid (36,122,163).

From the first, differences in the ionizing power of various solvents have seemed mysterious. However, it was recognized that these differences did not depend solely on the dielectric properties of the solvents, for some of the most ionizing of them such as sulfur dioxide and cresol possess relatively low dielectric constants (13.8 and 9.7 at 20°, respectively) (170, 249). Therefore, the solvent must exert a specific effect. von Baeyer thought in 1909 that the strong ionizing power of phenols (10) could be compared to the effect produced by a catalyst ("phenol transforms the chloride into an active state"). Naturally, he could not define this idea more accurately, as it was too advanced for the time. According to other authors (133), the ionization of triphenylmethyl halides could be a result of the interaction between the carbonium ion and the solvent. Facts argued against this interpretation, for, as Dilthey (112) pointed out, anhydrous (colored) crystalline carbonium salts were known, and it had been known for some time (147) that triphenylcarbonium ion solutions in sulfur dioxide lose their color on the addition of bases like ethers and pyridine. The disappearance of color was explained by the combination of the cationic center with the ether oxygen or pyridine nitrogen, a process represented in the following manner (112):

$$\underset{\substack{\text{colorless}\\ \text{nonpolar}}}{Ar_3CCl} \longrightarrow \underset{\substack{\text{colored}\\ \text{dipolar}}}{[Ar_3C]^+Cl^-} \xrightarrow{\text{Pyridine}} \underset{\substack{\text{colorless}\\ \text{dipolar}}}{[Ar_3CPy]^+Cl^-} \xrightarrow{H_2O} \underset{\substack{\text{colorless}\\ \text{nonpolar}}}{Ar_3COH}$$

Hammett was the first to present evidence that some solvents owe their great ionizing power to their ability to solvate the anion by hydrogen bonds or by other means, the cation being left relatively unsolvated. Of course, this result was not obtained by the methods of classical electrochemistry but by kinetic studies on the solvolysis of benzhydryl chloride in aqueous alcohol (130,332) (see below).

The discovery of triarylcarbonium salts brought back for consideration the Armstrong-Nencki quinoneimine structure (**1**) of triphenylmethane dyes, unanimously accepted in those early days. As far back as 1902 Gomberg (147) had suggested carbonium ion structures (**2**) for dyes such as malachite green, while a little later von Baeyer (8) introduced formulas



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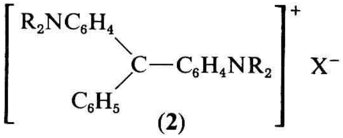

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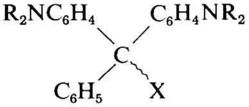

(3)

with "carbonium valencies" (**3**), which aimed to express the same thing but did so in a less successful manner. The carbonium ion formulation was extended to the extreme in the twenties by Dilthey and Wizinger, in the so-called "Bonner Farbentheorie" (396). Starting from the Wernerian con-