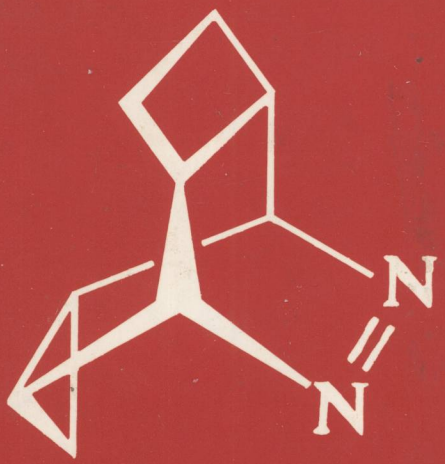
TOPICS IN APPLIED CHEMISTRY

CHEMICAL TRIGGERING

REACTIONS OF POTENTIAL UTILITY IN INDUSTRIAL PROCESSES



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Chemical Triggering

Reactions of Potential Utility in Industrial Processes

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Reactions of Potential Utility in Industrial Processes

TOPICS IN APPLIED CHEMISTRY

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CHEMICAL TRIGGERING
Reactions of Potential Utility in Industrial Processes
Gebran J. Sabongi

STRUCTURAL ADHESIVES
Edited by S. R. Hartshorn

For

Susan, Katie,
Odette, and Farid

with all my love

Preface

Chemical reactions which can, on demand, be switched on and off are valuable for industrial applications.

In order to make the best use of these reactions, it is essential to have them readily available for a research chemist. The chemical literature, in general, has not yet identified or grouped such reactions. However, their existence is relatively abundant.

This book is meant as a survey of those reactions which have potential utility in industrially useful processes. These reactions are grouped under the title of chemical release reactions which can be triggered by heat, light, electric current, etc., to release a specific compound from, or change in the physical or chemical properties of, a unimolecular reactant.

The book is divided into chapters covering ways to trigger the release of certain chemicals. Each chapter is further divided into sections, each beginning with a brief introduction of analogies of the discussed reactions and of how they were used in reported industrial processes.

This survey is not meant to be absolute or exhaustive but rather to be directive, to be as complete as possible, and to provide food for further thought.

G. J. Sabongi

St. Paul, Minnesota

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Introduction

The idea of putting together a monograph which could be used as a guide and reference for chemists in industry was born when I left academic life and moved into industry and applied research. The idea was also catalyzed by suggestions, interest, help, and unlimited support from Professor Alan R. Katritzky, a friend and my research advisor during my doctorate studies.

In applied industrial research, a number of processes are based on a few chemical reactions commonly used in academic research, which are viewed from a different angle. This difference is the concept behind this book. Could we put together a list of chemical reactions which are available in the chemical literature and would be valuable for industrial applications if viewed from a different perspective?

To do this, we had to define which of these reactions to include, the selection of their possible applications, and the conditions under which they would be utilized. After the survey of the common needs and a variety of industrially used reactions, it was apparent that chemical release reactions which can be triggered by a variety of triggering energies should be the main topic. The selection of their possible areas of application was a more difficult choice but it had to be narrowed to those which would utilize fine chemicals, such as image reproduction, information recording, and polymer applications, as opposed to bulk chemical applications.

The triggering conditions and nature of the triggering agent under which the chemical reaction would be used are determined by the nature of the application. Ideally, such reactions would be dormant in the absence of the triggering agent (energy) but would be triggered to completion in a short time under the action of the triggering energy.

Finally, the idea crystallized into a plan, which encompasses a survey of chemical reactions from the literature that, under specific triggering conditions, would release chemical reagents, including small molecules, acids, bases, and gases. These released chemicals could then be used in

industrially useful processes. No specific areas of potential use for such reactions will be discussed and it is left to the reader to determine their potential value. This approach was chosen in order to leave an element of inventiveness in any possible application.

The compilation of this survey is not meant to be absolute or exhaustive but directive and as complete as possible. The book is divided into chapters covering ways to trigger the release of certain chemicals. Each chapter is further divided into sections beginning with a brief introduction of analogies of the discussed reactions and how they were used in reported industrial applications. Such an introduction is meant to give the reader a quick and brief overview of areas of published applications. The rest of the sections of the chapter comprise a group of reactions which have in common the triggering agent (energy). The subsections include reactions which have in common the type of released molecule.

In order to make the best use of the included information, let us first define what is meant by triggered release. It is a chemical process which is switched on by the action of an energy, such as heat, light, or electric current, that causes the release of a specific chemical compound or the manifestation of a new physical property. The life of the reaction, and thus the release process, is limited to the time the triggering energy is switched on and ceases when the energy is switched off.

The thermally triggered release reactions surveyed are limited to those which proceed at temperatures between 70 and 200°C. These thermal limits eliminate processes which are unstable at room temperatures and those which require extreme temperatures in order to proceed. The ideal reaction is one which proceeds to completion in the shortest time and in high conversion yields. The common source for thermal energy is via conduction using a heated element, a liquid, or infrared radiation.

The reaction efficiency is described by the yield of the formed product expressed as a percentage and calculated as follows:

$$\text{Percent yield} = \frac{\text{Number of moles of product formed}}{\text{Number of moles of product theoretically possible}} \times 100$$

The photochemical processes have about the same requirements as the thermal ones. In general, most of the photochemical reactions are sensitive to ultraviolet radiation, and a few are sensitive to the energy from visible light. Some ultraviolet-sensitive reactions can be made sensitive to the energy of visible light by dye sensitization.

The efficiency of the reaction can be described by the quantum yield, which relates the amount of product released to the amount of energy absorbed. Mathematically the quantum yield is described as

$$\phi = \frac{\text{No. of moles of product formed (or reactants consumed)}}{\text{No. of Einsteins (moles) of light absorbed}}$$

If $\phi = 0$, all the absorbed energy is lost in physical processes and none is involved in the chemical reaction. When $\phi = 1$, the absorbed quanta are transformed stoichiometrically into product. When $\phi > 1$, a photo-induced chain reaction is occurring with an amplification factor.

The generation of the required photo energy can be accomplished by the use of a variety of sources. The most common are those which can provide a wide emission spectrum and thus have broad applicability. Examples are carbon arc, tungsten, mercury arc, pulsed xenon, and metal halide sources, whose emission spectra are graphically represented in Figure 1.

The use of optical filters in order to irradiate selectively at specific wavelengths is a well known technique which allows triggering at these wavelengths.

The low-pressure mercury lamp commonly used for photochemical release reactions has been recently studied by Hammond and Gallo[1] and its emission line at 253 nm examined as a function of mercury pressure, tube radius, and operating current.

Seliger and McElroy[2] and Calvert and Pitts[3] have published a range of chemical and other optical filters useful in selectively irradiated photochemical reactions.

Developments in photochemical instrumentation and techniques have been reviewed by West[4] and by McLaren and Shuger.[5] The latter review focuses on protein and nucleic acid photochemistry. Schonberg[6] has reviewed several light sources useful in photochemical reactions, their properties, manufacturers, emission wavelengths and corresponding energies.

Table 1 describes the emission energy of the mercury arc light source.

The recent commercialization of monochromatic lasers and laser diodes has allowed their use as another source of light energy. A laser beam can be described as a monochromatic, parallel, and coherent light beam which can deliver high light intensities by focusing the light output on a very small area. Seliger and McElroy[2] and Turro[8] have reviewed different aspects of lasers and their properties. Applications of lasers to chemistry have been periodically reviewed in the *Photochemistry: A Specialist Periodical Report* series of reviews[9] published by the Chemical Society of Great Britain.

The most commonly used lasers can be grouped into seven families:

1. Carbon dioxide lasers have the same active medium but are produced in four different configurations.
2. Chemical lasers have the same hardware which is used to obtain laser action from hydrogen fluoride or from its isotopic variants with emission at various wavelengths.

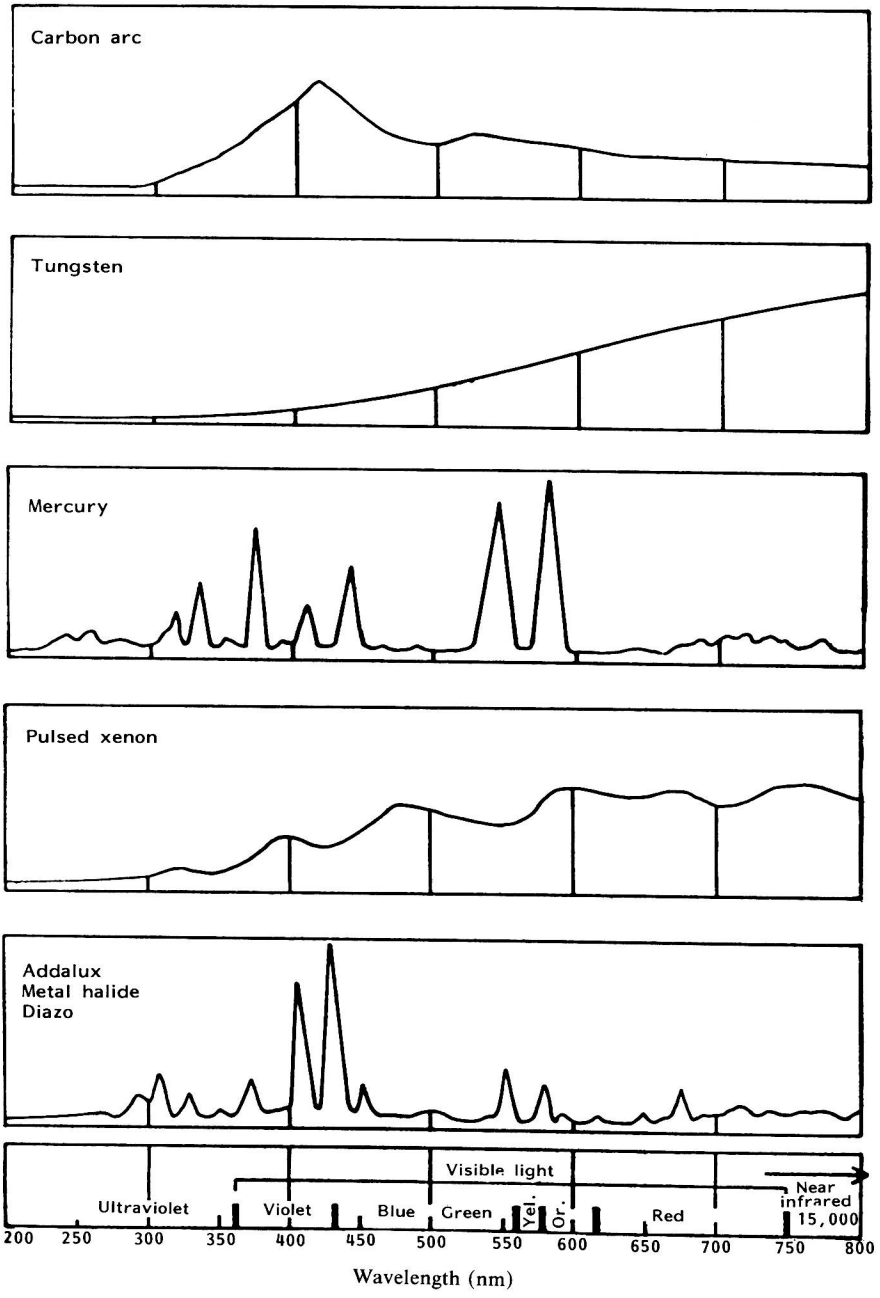

Figure 1. Spectral energy distribution of various light sources.

Table 1. Emission Energy from a Hanovia 679Å Lamp[a]

Mercury line (nm)	Radiated wattage
248.2	2.3
253.7	5.8
265.2	4.0
280.4	2.4
296.7	4.3
302.5	7.2
313.0	13.2
334.1	2.4
366.0	25.6
404.5	11.0
435.8	20.2
546.1	24.5
578.0	20.0

[a] Ref. 7.

3. Dye lasers rely on some organic dye, the active medium, in a liquid solvent and derive their energy from light emitted by different types of lasers or in some cases flash lamps. Their characteristics depend on the light source used.
4. Excimer lasers utilize different gases in the same hardware to produce light of different wavelengths.
5. Ion lasers emit light from ionized argon and/or krypton molecules; the hardware used to build them and mixed gas lasers is the same.
6. Semiconductor laser light is emitted at a p–n junction in a semiconductor diode; the wavelength depends on the semiconductor composition.
7. Solid-state lasers utilize light from a flash lamp or arc lamp to excite laser emission from atoms in a crystalline or glass host.

Table 2 contains further information on the typers of lasers available.

A number of currently available reviews provide excellent references in areas related to the subject matter of this volume, as well as detailed and complementary background information. In the areas of photo- and thermochemistry, reviews edited/authored by Bryce-Smith,[9] by Turro *et al.*,[10] by Srinivasan and Roberts,[11] by Henderson and Marsden,[12] by Schonberg,[6] by Brown,[13] by Zewail,[14] by Pappas,[15a] by Allen,[15b] by Hurd,[16] by Harrison and Harrison,[17] by Hodge and Sherrington,[18] by Greene,[19] and by McOmie[20] are useful.

Table 2. Lasers, Their Power and Wavelengths

Laser type	Output power	$\lambda_{max}^{emission}$ (nm)
Excimer		
Argon fluoride	10.0 W	193
Krypton fluoride	25.0 W	249
Xenon chloride	8.0 W	308
Xenon fluoride	7.0 W	351
Dye laser pumped by		
Nitrogen Excimer Neodynium-YAG	0.05-2.0 W	Tunable (300-1000)
Flash lamp	0.5-50.0 W	340-940
Ion laser	20-800 mW	400-900
Nitrogen	1-330 mW	337
Ion		
Argon	5.0 mW-20.0 W	Main lines, 486 and 514
Krypton	5.0 mW-20.0 W	Strongest, 647
Argon-krypton	0.5-6.0 W	450-670
Helium-cadmium	2-40 mW; 1.5-50 mW	442; 325
Helium-neon	0.1-50 mW	633-1152
Semiconductor diode		
Ruby	0.03-100 J	694
GaAs/GaAlAs	1-40 mW	780-905
Neodynium-YAG (pulsed)	400	1064
Neodynium-doped glass	0.15-100 J	1064
Neodynium-YAG (continuous)	0.04-600 W	1064
InGaAsP	1-7 mW	1100-1600
Chemical lasers		
Hydrogen fluoride	0.01-150 W	26.3×10^3
Deuterium fluoride	0.01-100 W	36.4×10^3
Carbon dioxide		
Flow gas	50-15,000 W	$9\text{-}11 \times 10^3$
Sealed tube	3-100 kJ	10.6×10^3
Pulsed TEA	0.03-75 J	$9\text{-}11 \times 10^3$
Waveguide	0.1-40 W	$9\text{-}11 \times 10^3$

Finally, errors of interpretation and fact are almost inevitable in a book of this nature. The responsibility for these is mine and I would appreciate having them brought to my attention.

The preparation of this book would not have been possible without the help of several people. I would like to express my appreciation to the 3M Company and its officers for their support, Professor Alan R. Katritzky whose encouragement, constructive suggestions, and review of the included material have been invaluable, and Dr. Melville R. Sahyun of the Science