

Oxygen-Containing Hydrocarbon Derivatives From Petroleum and Natural Gas

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Derivatives of petroleum and natural gas which contain oxygen are obtained primarily by oxidation, hydration, hydrolysis, and esterification, and the general literature on these processes, as well as on the Oxo, Synol, and Fischer-Tropsch processes, is presented. The literature concerning individual classes of oxygen-containing compounds and specific, important members of each class is next described. Catalytic operations are an inextricable part of many of the processes involved; attention is therefore directed to the literature on catalysis. Pertinent class numbers of the U. S. Patent Office are discussed. The literature presented is restricted to material published after 1936, although on occasion important earlier references are given.

Those derivatives of petroleum and natural gas which contain oxygen are obtained directly or indirectly from these basic hydrocarbons primarily by oxidation, hydration, hydrolysis, esterification, alkylation, and by hydrogenation of carbon monoxide. These processes either are generally applicable to the synthesis of many members of a specific class of oxygenated compounds, such as the synthesis of alcohols by hydration of olefins, or more frequently, give a mixture of oxygenated compounds of more than one class, e.g., oxidation and carbon monoxide hydrogenation. It is for this reason that the process literature is to be emphasized rather than the literature on individual compounds. An attempt will also be made to present selected literature on some individual compounds as well as on some groups of compounds. However, before considering the latter types of literature, attention must be directed to the general basic literature.

Basic Literature

The comprehensive treatment given the subject compounds by Ellis (26) has restricted the literature which is to be presented to material published after 1936, although on occasion important earlier references will be given. Emphasis has been placed on those publications which contain fairly extensive bibliographies, e.g., review articles and monographs.

Perhaps the most satisfactory method of quickly obtaining information on, and literature references to the desired oxygenated compounds is to refer to Kirk and Othmer's "Encyclopedia of Chemical Technology" (58). Although not yet complete, most of the oxygenated compounds and the processes used in their preparation are described in the volumes published. The importance of this work cannot be overemphasized. By consulting Thorpe (113) one can supplement information obtained from Kirk and Othmer. A new edition of Houben-Weyl (49) is in the process of publication and promises to be another important source of information.

Individual works of importance are Brooks (11), which appears to be the most com-

plete single volume in the field with respect to the oxygenated and other derivatives of aliphatic and naphthenic hydrocarbons; Goldstein (40); Faith, Keyes, and Clark (31), in which brief descriptions of commercial methods of preparation of many oxygenated compounds from hydrocarbons are given, although no literature references are cited; and finally Brooks and Dunston (12), which supplements information on old processes and deals also with subjects and processes which are new since 1937.

Review publications give considerable attention to the desired products. *Reports on the Progress of Applied Chemistry*, is published annually by the Society of Chemical Industry, London (91). Two sections of *Reviews of Petroleum Technology* (95), are of special interest—the section on derived chemicals and the section on petroleum literature. The latter section is concerned primarily with the nonperiodical literature, such as books and pamphlets. This first volume of *Progress in Organic Chemistry* contains a section, “Chemicals from Petroleum,” which emphasizes the oxygenated derivatives (89).

A special guide to the publications known as PB, FIAT, and BIOS reports, many of which are included in references to the literature, is provided in the *Bibliography of Technical Reports* (115). Lederman and Green (64) give a more detailed explanation of such publications.

Many other encyclopedias, books, and review publications could be mentioned, but the above-mentioned publications are deemed essential to the location of the desired literature on the oxygenated compounds.

Process Literature

The process literature is presented in some detail in the work by Shreve (105), and especially by Groggins (42). Earlier work on oxidation processes is adequately dealt with in the AMERICAN CHEMICAL SOCIETY Monograph by Marek and Hahn (69).

The September 1948 issue of *Industrial and Engineering Chemistry* contained the first Unit Processes review. This first review embraced developments in unit processes reported in the literature since approximately the start of World War II. Among the the pertinent processes covered by the first review were oxidation, hydration and hydrolysis, esterification, alkylation, halogenation, and sulfonation. Thereafter, these reviews appeared annually with the exception of the hydration and hydrolysis section which appeared biennially. The section on hydrogenation and hydrogenolysis first included the hydrogenation of carbon monoxide in 1951. The literature surveyed by these process reviews is very extensive and considers not only the journal literature, but the patent and PB literature as well. These reviews, in addition to providing the most expedient method for keeping abreast of the current literature for the processes involved, serve as a fairly comprehensive literature source for the time period covered by all the reviews.

Much of the literature through 1947 on the preparation of oxygenated compounds by the hydrolysis as well as by the dehydrochlorination of organic chlorine compounds is contained in a work by Huntress (51).

Variations in the conditions employed in the hydrogenation of carbon monoxide have led to a group of processes all of which yield important quantities of oxygenated materials, either as by-products or as the main product, the initial carbon monoxide and hydrogen mixture (synthesis gas) being derivable from paraffin gases, especially methane. Two of these processes, although directed primarily to the manufacture of synthetic fuels, have always given considerable amounts of by-product oxygenated materials. These are the Fischer-Tropsch process and the American hydrocarbon process (Hydrocol process). Those processes concerned directly with the production of oxygenated compounds are the methanol and higher alcohol syntheses, the Synol process, and the recent Oxy process. A recent paper describes a British process in which the amount of oxygenated compounds obtained is intermediate to that obtained in the processes mentioned above. The Oxo process, that is, the catalytic addition of carbon monoxide and hydrogen to olefins to give aldehydes followed by reduction of the latter to alcohols, is almost invariably associated with carbon monoxide hydrogenation in the literature and will be similarly treated here.

Publications by Storch, Golumbic, and Anderson (110), U. S. Naval Technical Mission (118), Schmidt (99), Martin and Weingaertner (70), Anderson (4), Weil and Lane

(123), and Komarewsky, Riesz, and Estes (60) include discussions of the majority of the above-mentioned processes except the Oxyl.

Recent papers by Eliot (25), Steitz and Barnes (109), Cain, Weitkamp, and Bowman (15), Weitkamp and Frye (124), and Morrell (78) are concerned with the distribution of oxygenated compounds in the Hydrocol products; a paper by Gall, Gibson, and Hall (36) discusses the British counterpart.

Considerable literature, especially patent literature, deals with processes for the isolation of oxygenated products present in the mixture of hydrocarbons and oxygenated compounds obtained from synthetic fuel processes. An excellent source for such literature, as well as for much carbon monoxide hydrogenation and Oxo process literature, is the U. S. Bureau of Mines, "Synthetic Liquid Fuel Abstracts," now discontinued (114). Although general and patent literature are included therein, probably the greatest importance of this work lies in the fact that abstracts are given for German work—that is, the PB reports, the TOM (Technical Oil Mission) reels, etc., whereas *Chemical Abstracts* has not abstracted such material, and the *Bibliography of Technical Reports* abstracts are often inadequate and poorly indexed by comparison.

Special references on the methanol and higher alcohol syntheses are Ellis (27), Hirst (45), Kastens (54), and Giesen and Hanisch (38). The Oxyl process is described by Roelen and Beery (96). The Synol process literature is covered in references (4, 38, 110, 118). Oxo synthesis literature is reported on in some detail by Holm (46), Schuster (100), and Orchin and Schroeder (83).

Recent research on acetylene as the basic hydrocarbon in the synthesis of a number of important oxygen-containing compounds has centered on the work of Walter Reppe and his associates of Germany. Prior to Reppe's work, the most important oxygen-containing derivatives of acetylene were acetaldehyde and acetone.

Three important processes have evolved from Reppe's work. Vinylation, the formation of vinyl derivatives by reaction of such compounds as acids, glycols, and alcohols with acetylene, produces the important vinyl esters and vinyl ethers. Ethinylation is defined as the reaction of acetylene with the carbon atom of a reactant without loss of the triple bond. A major application of the ethinylation reaction is to aldehydes and ketones to give alkynols and alkyndiols—e.g., the reaction of acetylene with formaldehyde to give propargyl alcohol and butyn-2-diol-1,4. Carboxylation (also referred to as carbonylation), the reaction of acetylene with carbon monoxide in the presence of metal carbonyls, has been applied to the production of acrylic acid, acrylates, and hydroquinone.

The polymerization of acetylene to cyclooctatetraene and oxygenated derivatives obtainable from the latter is also described (17, 44, 84, 92, 93, 94).

The general acetylene literature up to 1938 is reported on by Nieuwland and Vogt (81). In addition to a translation of Reppe's own work (92), two excellent reviews in the English language of Reppe chemistry are Owens and Johnson (84) and Copenhagen and Bigelow (17). Several other important works on Reppe chemistry are Reppe (93, 94), Hecht and Kröper (44), and Piganiol (86).

The Diels-Alder reaction (diene synthesis) is the addition of compounds containing double or triple bonds (dienophiles) to the 1,4 positions of conjugated dienes with the formation of six-membered hydroaromatic rings. Hydrocarbons most often used in the reaction are 1,3-butadiene, cyclopentadiene, and isoprene, and dienophiles used include maleic anhydride, acrolein, and acrylic acid. The literature on this process is thoroughly reviewed by Alder (1), Kloetzel (59), Holmes (48), and Norton (82).

The reaction of olefins with aldehydes to form 1,3-glycols has recently been reviewed by Arundale and Mikeska (5).

Considerable literature exists on the mechanism of hydrocarbon oxidation and auto-oxidation. The more important of these works are by Waters (122), the Faraday Society (23, 32), and Frank (33).

Organic peroxide formation by the oxidation of hydrocarbons and the reaction of these compounds is especially emphasized by Frank (33), Criegee (18), Hawkins (43), and Kharasch (57).

The literature on the use of organic per acids for the oxidation of olefins, especially higher olefins, to epoxides and glycols has been surveyed by Swern (112).

Oxidation of hydrocarbons with selenium dioxide can result in the formation of dialdehydes, ketones and diketones, and unsaturated alcohols, depending upon the hydrocarbon used. Such oxidations have been summed up by Rabjohn (90).

Since so many of the processes involved are catalytic in nature, a few of the more important publications in the field of catalysis should be mentioned. These are Berkman, Morrell, and Egloff (6), Burk (14), Griffith (41), Schwab (101), the Faraday Society (22), and Frankenburg (34).

A guide to the analysis, as well as to the ordinary physical properties of pure oxygenated compounds is provided for in a work by Huntress and Mulliken (52). The physical constants (n_D^{20} , b.p., and m.p.) with references to the original literature for a selected number of organic peroxides are given by Mesrobian (71).

Literature on Individual Compounds or Groups of Compounds

The following literature has been selected as a guide to information on a few individual members and groups of oxygenated compounds. These compounds have been chosen either because special literature is available or because of their importance. The German reports included have been chosen since they give detailed information not generally obtainable. For many of the individual members and groups of compounds, the existing literature is almost exclusively patent literature. The pertinent classes of the U. S. patent system will be described later.

Formaldehyde. Oxidation with air or oxygen of natural gas or propane and butane yields not only formaldehyde but also acetaldehyde, propionaldehyde, acetone, methyl ethyl ketone, tetrahydrofuran, methanol, propanol, butyl alcohols, and formic, acetic, and propionic acids. Such literature is covered by Walker (120, 121). Two reports on German processes for oxidation of methane to formaldehyde are given by Sherwood (104), and by Holm and Reichl (47). One of these processes indicates the almost exclusive formation of formaldehyde; it is also indicated that the process was applied to ethane and propane with similar results.

Acetaldehyde. The manufacture of acetaldehyde in Germany by hydration of acetylene is described by Alexander (2) and by Brundrit, Taylor, and Ellis (13). Acetaldehyde preparation by hydrolysis of lower vinyl ethers is briefly indicated in the latter reference as well as by Leaper and Direnga (63). For complete coverage of the literature on these methods, see references (17, 44, 81, 84, 86, 92, 93, 94).

Ethyl Alcohol and Higher Alcohols. Two general processes exist for hydrating olefins to alcohols. The first is by absorption of olefins in inorganic acids, primarily sulfuric acid, followed by hydrolysis of the intermediate ester. The second process is the direct catalytic hydration of the olefin. The literature on these processes, especially as applied to ethanol and 2-propanol manufacture, is well covered in the general works listed above, and especially by Brooks (11). German work on the catalytic hydration of olefins is described by Kammermeyer and Carpenter (53). The preparation of amyl alcohols via chlorination of pentanes and hydrolysis of the halides is described by Kenyon (56).

Epoxides and Glycols. The literature on the important aliphatic epoxides and glycols, especially ethylene and propylene oxides and ethylene and propylene glycols, is given by Curme and Johnston (20). Detailed descriptions of German processes for the manufacture of ethylene oxide by direct oxidation of ethylene and via chlorohydrination of ethylene are given by Goepf (39) and by Vaughan and Goepf (119). Brief descriptions of the direct and chlorohydrination processes as well as of the manufacture of ethylene glycol from ethylene oxide by hydration and from ethylene dichloride by hydrolysis are given by Morley (77). The hydration of ethylene oxide to ethylene glycol and higher glycols is also described by Brandner and Goepf (9).

Allyl Alcohol and Glycerol. These two products are treated together since both involve the chlorination of propylene to allyl chloride. The Shell allyl alcohol process is described by Fairbairn, Cheney, and Cherniavsky (30). This same process and the glycerol process are described by Williams (125). The German counterpart of these

processes is briefly described by Sheely (102). Allyl alcohol preparation by isomerization of propylene oxide is given by Lunsted (68). The Shell Chemical Co. has published a booklet (103), which describes the properties and reactions of this alcohol. Further literature on synthetic glycerol is to be found in the new AMERICAN CHEMICAL SOCIETY Monograph by Miner and Dalton (73).

Acetone, Methyl Ethyl Ketone, Acetic Acid, and Propionic Acid. Oxidation of the lower hydrocarbons in the gas phase catalyzed by hydrogen bromide gives carboxylic acids, ketones, and hydroperoxides, depending on the hydrocarbon used. Ethane gives acetic acid; propane gives acetone plus a significant amount of acetic and propionic acids; *n*-butane yields methyl ethyl ketone and acetic acid. Oxidation of branched-chain hydrocarbons such as isobutane and isopentane gives peroxides and hydroperoxides as major products and alcohols as coproducts. This literature is reviewed by Rust and Vaughan (97). For information on acetone from 2-propanol, see the general introductory literature. For literature on acetone via cumene oxidation, see below under phenol from cumene.

Carboxylic Acids and Esters. The literature on German methods for the preparation of unsaturated acids and their esters via acetylene, carbon monoxide, and water or alcohol, as well as the application of this reaction to olefins, carbon monoxide, and water or alcohol to give saturated acids and esters, is to be found in references (17, 44, 84, 92, 93, 94). Other references on these methods are Blair-McGuffie (7) and Natta (80). The preparation, properties, and reactions, especially polymerization, of products from the acetylene-carbon monoxide reaction, such as acrylic acid and its esters, are given by Blout and Mark (8) and by Schildknecht (98). Similarly treated therein are the vinyl esters from acetylene and carboxylic acids, and other vinylation products such as vinyl ethers. The esterification of organic acids with olefins is reviewed by Morin and Bearse (76).

Higher Fatty Acids. Oxidation of higher paraffins can give mixtures of acids, alcohols, and carbonyl compounds, although fatty acids may be obtained as the principal product. Publications by Wittka (126), Stossel (111), Allen (3), Lanning (62), Zabel (128), and Gall (35) are of importance in this field.

Adipic Acid. The German process for the preparation of this compound is described by Smith (108).

Maleic Anhydride. The preparation of maleic anhydride from C₄ hydrocarbons is given by Bretton (10). The preparation of maleic anhydride from benzene is described in Faith, Keyes, and Clark (31). Maleic anhydride is an important by-product in the phthalic anhydride process.

Phthalic Anhydride. The preparation of phthalic anhydride from xylene is described by Parks and Allard (85) and Levine (65). Phthalic anhydride from naphthalene is discussed by Downs (24), Shreve and Wilborn (106), Ellis (28), Hunter (50), Young (127), and Nash (79).

Phenol. The manufacture of phenol by the oxidation of benzene is described by Denton (21) and by Simons and McArthur (107). The literature on phenol by the oxidation of cumene is partly covered in the reports of Frank (33), Hawkins (43), and Kharasch (57), mentioned earlier. A brief description and flow sheet of the process is given in *Chemical Engineering* (16). The patents in this field are mainly held by The Distillers Co., Ltd., Hercules Powder Co., and Allied Chemical and Dye Corp. In this phenol process large amounts of acetone are obtained as a coproduct. It should also be noted that the process may be directed to the production of cumene hydroperoxide and α,α -dimethylbenzyl alcohol. Krieble (61) and Kenyon and Boehmer (55) describe the preparation of phenol by the chlorination and sulfonation processes.

Alkyl Phenols. The literature on the alkylation of phenols with olefinic hydrocarbons has been reviewed by Price (88).

Aromatic Aldehydes. The preparation of aromatic aldehydes from benzene or monoalkyl and polyalkyl aromatic compounds by means of carbon monoxide and hydrogen chloride has been reviewed by Crounse (19).

Acetophenone. The oxidation of ethylbenzene to acetophenone is described by Emerson (29) and by Pinkernelle and Kroning (87).

Aromatic Acids by Oxidation of Side Chains. German work on this subject is briefly reported on by Mittag (74, 75) and by Michel and Krey (72).

Cresylic Acids. These compounds are discussed by Gallo (37).

Naphthenic Acids. Important literature on these acids includes Littmann and Klotz (66) and Lochte (67). Dr. Lochte is preparing a book entitled "Petroleum Acids and Bases"; publication is expected in late 1953 or early 1954.

U. S. Patent Literature

The U. S. Patent Office provides several guides for obtaining those patents of interest. These are the "Manual of Classification of Patents" (117), the index to said manual, plus a series of classification bulletins which define the classes and subclasses listed in the manual. Once having determined the subclasses of interest, one may obtain from the Patent Office, at a charge of about 20 cents a page, separate numerical lists of both the original references and cross references in each subclass. Furthermore, the Patent Office will supply these lists of subclasses and cross-reference lists upon receiving a request which fully describes the subject matter of interest. The subclasses of Class 260, "The Chemistry of Carbon Compounds," are the subclasses of main interest, and these have been recently revised. The definitions for Class 260 are in *Classification Bulletin* No. 200 (116). It may be noted at this time that a revised copy of this bulletin, as well as a new index to the "Classification Manual," is scheduled for publication in the near future.

Specific important subclasses of Class 260 are listed.

Heterocyclic compounds

- 341 Polycarboxylic acid anhydrides
- 342 Polycarboxylic acid anhydrides by oxidation of aromatic compounds, e.g.—phthalic anhydride from naphthalene or *o*-xylene and also maleic anhydride from benzene
- 342.6 Anhydrides of acyclic polycarboxylic acids
- 348 Epoxy compounds, general
- 348.5 Epoxy compounds by oxidation of olefins—e.g., ethylene oxide by oxidation of ethylene
- 348.6 Epoxy compounds by dehalogenation (actually dehydrohalogenation)—e.g., ethylene oxide from ethylene chlorohydrin

Carboxylic or acyclic compounds

- 449 Hydrogenation of carbon oxides to give mixtures of hydrocarbons, alcohols, esters, and acids
- 449.5 Methanol synthesis from CO and H₂. Higher alcohol synthesis from CO and H₂ are also included in this subclass
- 449.6 Hydrogenation of carbon oxides with iron, cobalt, or nickel catalysts (Fischer-Tropsch process). Hydrocarbons are the main products
- 450 Recovery and separation of oxygenated products obtained from CO and H₂
- 451 Partial oxidation of nonaromatic hydrocarbon mixtures, e.g., petroleum, paraffins, and natural gas, to produce a mixture of products, such as esters, acids, aldehydes, ketones, and alcohols. This also includes higher fatty acids from petroleum and patents on formaldehyde production
- 452 Subclass 451, in which the recovery or purification of the products is especially emphasized
- 460 Sulfuric acid esters from olefins by direct sulfation
- 468 Carboxylic acid esters
- 478 Acyclic carboxylic acid esters
- 497 Acyclic carboxylic acid esters from olefins; this includes esters from olefins + alcohol + CO and from olefins + acids
- 498 Acyclic carboxylic acid esters from acetylene; this includes esters from acetylene + acid
- 514 Carboxylic acids; this includes naphthenic acids
- 515 Aromatic carboxylic acids
- 524 Aromatic side chain alkyl group oxidation—e.g., toluene oxidation to benzoic acid and *p*-xylene oxidation to terephthalic acid
- 526 Acyclic carboxylic acids, general
- 530 Acyclic carboxylic acids by oxidation of aldehydes
- 533 Acyclic carboxylic acids from single or mixed hydrocarbons of known constitution; this includes reaction of acetylene with CO and water, reaction of olefin with CO and water, and also dibasic acids from cycloalkanes
- 537 Acyclic polycarboxylic acids, e.g., from cycloalkanols and/or cycloalkanones
- 540 Saturated lower fatty acids, general

- 542 Formic acid from CO and water
- 546 Carboxylic acid anhydrides, general
- 586 Carbocyclic or acyclic ketones—e.g., by oxidation of cycloalkanes
- 590 Aromatic ketones
- 592 Acetophenone
- 593 Acyclic ketones
- 596 Dehydrogenation or dehydration of alcohol to form ketones, e.g., acetone from isopropyl alcohol
- 597 Acyclic ketones from hydrocarbons; this includes ketones prepared by the Oxo process
- 598 Carbocyclic or acyclic aldehydes
- 599 Aromatic aldehydes
- 601 Acyclic aldehydes
- 604 Acyclic aldehydes from hydrocarbons—processes where definite hydrocarbons are employed as starting material; this includes Oxo process, formaldehyde processes and acrolein from propylene
- 605 Acyclic aldehydes from acetylene—e.g., acetaldehyde from acetylene
- 610 Organic carbocyclic or acyclic peroxides—e.g., cumene hydroperoxide
- 611 Carbocyclic or acyclic ethers
- 614 Acyclic ethers
- 617 Carbocyclic or acyclic hydroxyl compounds, general
- 618 Aromatic hydroxy compounds
- 619 Phenols
- 621 Phenol by benzene oxidation
- 624 C-polycarbon alkyl or alkylene phenols
- 626 C-isopropyl or isopropylene phenols; both 624 and 626 include patents on alkylation of phenols
- 628 Phenols from aryl sulfonates
- 629 Phenols by hydrolysis of aryl halides
- 631 Cyclohexanols
- 632 Acyclic hydroxy compounds (see also 638); this includes Oxo process patents which go beyond the aldehyde stage by reduction
- 634 Acyclic chlorohydrins from olefins
- 635 Polyhydric acyclic compounds; this includes oxidation of cycloalkanes, cycloalkanol and cycloalkanones to such products
- 636 Polyhydric acyclic compounds by hydrolysis of alkyl polyhalides or halohydrins—e.g., the glycerol process and ethylene glycol from ethylene dichloride
- 637 Purification of acyclic polyhydric compounds
- 638 Acyclic hydroxyl compounds directly from carbonyl containing compounds; this seems to overlap Subclass 632 as far as the Oxo process alcohols are concerned
- 639 Acyclic hydroxy compounds by hydrolysis of alkyl esters of polybasic inorganic acids—e.g., alcohols via olefins + inorganic acid + hydrolysis
- 640 Acyclic hydroxy compounds by hydrolysis of alkyl halides
- 641 Acyclic hydroxy compounds by hydration of olefins (direct hydration)
- 643 Purification or recovery of acyclic hydroxy compounds
- Processes
 - 686 Sulfonation or sulfation
 - 687 Oxidation
 - 690 Hydrogenation
 - 692 Etherification by alkylation of an alcoholic or phenolic hydroxyl group
 - 693 Fusion with alkalis to convert sulfonic group to OH group
 - 694 Halogenation

Close examination of the above list will reveal that both the original subclass and the cross references in each of several subclasses must be consulted in order to find all the art on a given subject. It should also be noted that frequent changes in the classification scheme are made.

General Sources

To obtain references to the foreign patent literature one must search through either *Chemical Abstracts*, *Chemisches Zentralblatt*, or *British Abstracts*. To obtain literature on other pertinent German processes, the *Bibliography of Technical Reports* must be searched. It is hoped that the literature which has been presented will provide a background for such searches and also indicate some of the more numerous headings which will have to be used to obtain a more complete picture of the literature of the oxygen-containing hydrocarbon derivatives obtainable from petroleum and natural gas.

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