

theses of these systems have so far been unsuccessful [103,104].

Compound (73), like (74), may lack the postulated resonance stabilization, since the properties of (74) and its derivatives can be satisfactorily explained by the structure with substantially localized double bonds [105,106]. In the case of (75), the resonance energy is probably consumed by the enormous ring-strain energy; this is shown by the fact that (75) can also be described as a valence isomer of a *m*-dehydrobenzene.

IV. Conclusion

The chemistry of the cyclopropenylum compounds is only eight years old. In this short period, however, the important questions have already been answered, so that only a few problems of synthesis remain unsolved, viz.

[103] H. Prinzbach and W. Rosswog, *Angew. Chem.* 73, 543 (1961); H. Prinzbach, personal communication.

[104] B. Föhlisch, *Chem. Ber.* 97, 88 (1964).

[105] H. Prinzbach, *Angew. Chem.* 76, 235 (1964); *Angew. Chem. internat. Edit.* 3, 319 (1964).

[106] T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Japan* 35, 910 (1962).

the unsubstituted cyclopropenylum cation (1), the benzocyclopropenylum cation, and bicyclo[3,1,0]hexatriene (75).

The preparation of the substituted cyclopropenylum salts, cyclopropenones, and methylenecyclopropenes has extended the number of the "Hückel aromatic" systems. The study of their properties and reactivities has impressively demonstrated the expected relationship with the "Hückel homologous" seven-membered ring compounds. If equality of the bond lengths and the existence of a ring current are accepted as criteria of aromatic character, the cyclopropenylum salts deserve to be called aromatic compounds.

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Syntheses of Oxide Halides

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Knowledge of the oxide halides has made significant advances in recent years as a result of new methods of preparation. Moreover, the systematic study of older methods has led to versatile syntheses which permit the preparation of many new oxide halides. A brief outline of the scope, limitations, and difficulties of the various processes is given together with a number of examples.

I. Partial Hydrolysis of Halides

Although the method of partial hydrolysis of halides has been known for a very long time it can only be used in special cases to prepare definite anhydrous oxide halides. The reaction proceeds according to the General Equation (a).



However, the course of such hydrolyses is greatly complicated by the fact that other reactions, such as the formation of stable hydrates, oxyacids of the halides, hydroxo compounds, oxides, etc. are also formed in many cases. The method can, therefore, be successful only if the reaction product is somehow stabilized or removed, e.g. by making use of its volatility. Examples are found in the preparations of POCl_3 [1]

[1] C. A. Wurtz, *Ann. Chim. physique* 20, 472 (1847).

from PCl_5 , of $\text{P}_2\text{O}_3\text{Cl}_4$ [2] from POCl_3 , or of the silicon oxide halides of general formula $\text{Si}_n\text{O}_{n-1}\text{Cl}_{2n+2}$ which can be obtained by partial hydrolysis of SiCl_4 , and of which the representatives up to $n=10$ have been isolated [3-7].

Oxide halides can also be stabilized in the crystal lattice. In such cases partial hydrolysis of the halide can even be carried out with excess water. This group includes certain oxide halides of mercury, e.g. $2\text{HgCl}_2 \cdot \text{HgO}$ [8]. In addition to the homopolar character of the Hg-X

[2] E. Fluck, *Angew. Chem.* 72, 752 (1960).

[3] R. Rheinboldt and W. Wisfeld, *Liebigs Ann. Chem.* 517, 197 (1935).

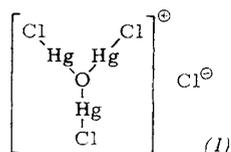
[4] W. C. Schumb and D. F. Holloway, *J. Amer. chem. Soc.* 63, 2753 (1941).

[5] W. C. Schumb and A. J. Stevens, *J. Amer. chem. Soc.* 69, 726 (1947); 72, 3178 (1950); 75, 1513 (1953).

[6] J. Goubeau and R. Warncke, *Z. anorg. allg. Chem.* 259, 109 (1949).

[7] F. K. Scholl, Ph. D. Thesis, Technische Hochschule Stuttgart, 1960.

bond, the high symmetry of complex structural groups is also found to be a stabilizing factor in these compounds [cf. Formula (1)].



The method of partial hydrolysis of halides is particularly successful in the preparation of the oxide halides of the trivalent elements antimony, bismuth, indium, the rare earths, and some actinides. All these oxide halides are structurally related, and presumably the lattice is a stabilizing factor here, in that it prevents complete hydrolysis by steric effects.

The oxide fluorides of the rare earths, MOF, have been found to possess an unusually high thermal stability; they are prepared by partial hydrolysis of the trifluorides at 800 °C in a current of moist nitrogen [9–11]. The formation of higher oxides of cerium and praseodymium as by-products can be suppressed by admixture of a little hydrogen or ammonia with the carrier gas [10].

The oxide fluorides NbO₂F and TaO₂F can be prepared by simply drying solutions of niobium and tantalum pentoxides in hydrofluoric acid [12]. However, it should be pointed out that it is very difficult to obtain products which are completely free of OH⁻ ions by this method. For example, when a solution of Ti⁴⁺ in hydrofluoric acid is dried, the product is a "TiOF₂" [13] which can have an OH content of up to 50 % of the fluorine content, and which must, consequently, be formulated as TiO(OH)F [14]. This compound still retains the ReO₃-type lattice of TiOF₂ [15], owing to the practically equal ionic radii of OH⁻ and F⁻.

Finally, the partial hydrolysis method still enjoys a certain importance in the preparation of a number of oxide chlorides, oxide bromides, and oxide iodides of the rare earths and actinides. Whereas ammoniacal hydrolysis is used in the preparation of the oxide chlorides and oxide bromides of these elements [16–19], the oxide iodides MOI (M = La, Sm, Tm, Y, Ac, Pu) can be prepared by simply heating the triiodides in moist air [20–22].

[8] A. Weiss, G. Nagorsen, and A. Weiss, *Z. anorg. allg. Chem.* 273, 151 (1953).

[9] S. Fried, F. Hagemann, and W. H. Zachariasen, *J. Amer. chem. Soc.* 72, 772 (1950).

[10] A. I. Popov and G. E. Knudson, *J. Amer. chem. Soc.* 76, 3921 (1954).

[11] A. Zalkin and T. H. Templeton, *J. Amer. chem. Soc.* 75, 2453 (1953).

[12] L. K. Frevel and H. W. Rinn, *Acta crystallogr.* 9, 626 (1956).

[13] K. S. Vorres and F. B. Dutton, *J. Amer. chem. Soc.* 77, 2019 (1955).

[14] K. Dehnicke, unpublished work.

[15] K. S. Vorres and J. Donohue, *Acta crystallogr.* 8, 25 (1955).

[16] F. A. Bannister and M. H. Hey, *Mineralog. Mag. J. mineralog. Soc.* 24, 49 (1935).

[17] L. G. Sillen, *Svensk. kem. Tidskr.* 53, 39 (1941).

[18] W. H. Zachariasen, *Acta crystallogr.* 2, 388 (1949).

[19] B. B. Cunningham, *Microchem. J.*, Symposium Issue, p. 69–93 (1961).

[20] L. G. Sillen and A.-L. Nylander, *Svensk. kem. Tidskr.* 53, 367 (1941).

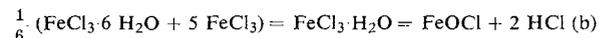
[21] F. H. Kruse, L. B. Asprey, and B. Morosin, *Acta crystallogr.* 14, 541 (1961).

[22] L. B. Asprey and F. H. Kruse, *J. inorg. nuclear Chem.* 13, 32 (1960).

The extent to which halides can be subjected to partial hydrolysis has been explored in many directions. Mention is made only of the unsuccessful attempts to prepare ZrOCl₂ [23–25], or the surprising course of the hydrolysis of TaCl₅ [26,27], which – in contrast to NbCl₅, which yields NbOCl₃ – leads not to an oxide chloride, but exclusively to Ta₂O₅; this reaction can be used for the separation of niobium and tantalum [28].

II. Special Cases of the Partial Hydrolysis of Halides

A number of oxide halides can be obtained by controlled thermal decomposition of definite hydrates; it should be noted, in this connection, that hydration may be assumed to be a primary step in hydrolysis. For example, the thermal decomposition of FeCl₃·6H₂O, after mixing with 5 moles of FeCl₃, leads to the elimination of HCl to yield FeOCl [29], as shown in Equation (b).



In special cases a partial hydrolysis can be combined with an oxidation or a reduction. In this way the oxide halides EuOI [30] and PuOF [31] are obtained by oxidizing hydrolysis of EuI₂ in an oxygen atmosphere, or reducing hydrolysis of PuF₄ with atomic hydrogen.

Instead of the controlled thermal decomposition of halide hydrates, it is possible in many cases to use the thermal decomposition of definite etherates. Thus the thermal decomposition of the monoetherates of NbCl₅, NbBr₅, and TaCl₅ starts at 90 °C with the elimination of ethyl halide to yield the solvate-free oxide halides NbOCl₃ [see Equation (c)], NbOBr₃, and TaOCl₃ [32].



III. Commutation [*] of Oxides and Halides

By far the most important method for the preparation of oxide halides is the thermal combination of a halide with the corresponding oxide [see Equation (d)].



[23] P. Schmid, *Z. anorg. allg. Chem.* 167, 369 (1927).

[24] E. Chauvenet, *C. R. hebdom. Séances Acad. Sci.* 154, 821 (1912).

[25] S. Takagi, *J. chem. Soc. Japan, Pure Chem. Sect.* 75, 637 (1954).

[26] H. Schäfer and H. Bosch (1952), unpublished work.

[27] H. Schäfer, *Angew. Chem.* 71, 157 (1959).

[28] German patent 1017601 (1959), Inventor: W. Schornstein and F. Kern.

[29] H. Schäfer, *Z. anorg. allg. Chem.* 260, 279 (1949).

[30] H. Bärnighausen, *J. prakt. Chem.* 14, 313 (1961).

[31] J. Karle, cited by W. H. Zachariasen, *Acta crystallogr.* 4, 231 (1951).

[32] F. Fairbrother, A. H. Cowley, and N. Scott, *J. less-common Metals* 1, 206 (1959).

[*] It seems reasonable to use the term "commutation" to describe the reverse of a "dismutation" in which no redox reaction occurs.



The term "comproportionation" will always be used to describe the reverse of a "disproportionation", in which a redox reaction is involved.



This method has recently gained considerably in importance and versatility, both practically and theoretically, as a result of the extensive studies by Schäfer [33] on chemical transport reactions. The limitation of this method is that the reaction of the halide with the oxide must proceed at a lower temperature than the decomposition of the expected oxide halide. Whereas the problems encountered in the preparation of oxide halides by partial hydrolysis are predominantly kinetic, thermodynamic effects come to the fore in this case. Most of the compounds involved have a high thermal stability.

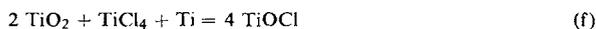
The commutation method is very useful for the preparation of the oxide fluorides of the rare earths, MOF [11,34–38], the high thermal stability of which has already been seen from their preparation by partial hydrolysis at 800 °C.

The importance of the detailed study of the thermodynamic relationships in such oxide/halide systems can be clearly seen from thermal equilibrium measurements on the system Ta₂O₅/TaCl₅ which exists in equilibrium with gaseous TaOCl₃ at temperatures above 500 °C [39]. On cooling, the reverse reaction occurs and TaOCl₃ decomposes; however, the composition of TaOCl₃ can be confirmed by other methods [32,40]. In the case of niobium, NbOCl₃ [41] and Nb₃O₇Cl [42] can be obtained by simple commutation of the oxide and the halide, with preparatively useful results.

The commutation method can sometimes also be modified to give oxide halides of intermediate valence states. Thus TiOCl [43] is prepared by “comproportionation”, either from TiO₂ and TiCl₃ according to Equation (e),



or by the addition of metallic titanium to a TiO₂/TiCl₄ mixture [Equation (f)].



A completely analogous method can be used for the preparation of VOCl [44] and CrOCl [45], both of which crystallize in the same lattice as FeOCl which is rather less stable thermally, and consequently cannot be prepared by this method [44–46]. The comproportionation method can be used for the preparation of NbOCl₂

[42] and TaOCl₂ [42] by adding metallic niobium or tantalum in stoichiometric amounts to the oxide/halide mixture. It is possible to obtain ReOCl₄ [47] from Re₂O₇ and ReCl₅ at 70 °C by a particularly careful comproportionation, although excess Re₂O₇ leads to the formation of ReO₃Cl [47].

In the case of the elements of the main groups whose oxide halides can be prepared by the commutation method, the temperatures used are generally rather low, and furthermore, thermally unstable compounds are often encountered. However, low temperatures necessitate the use of reactive oxides, such as are found in the case of the elements boron, phosphorus, arsenic, sulfur, and selenium. Thus B₂O₃ dissolves in BCl₃ to form the cyclic trichloroboroxole (BOCl)₃ [48,49], and As₂O₃ dissolves in AsCl₃ to form the open-chain polymer (AsOCl)_m [50]. BF₃ and BBr₃ can also be reacted with B₂O₃ above 250 °C and under pressure to form trimers, namely the trihalogenoboroxoles, the products decomposing again into the starting materials on slow cooling [48,49]. By rapid cooling, however, it is possible to obtain (BOF)₃ which is stable below –125 °C [51]. Owing to the low reactivity of Al₂O₃, a temperature of 440 °C is required for the preparation of AlOBr [52], while the corresponding gallium oxide halides, GaOX, with the exception of GaOF, can all be prepared from GaX₃ and Ga₂O₃ between 300 and 400 °C [53].

IV. Reactions of Halides with Oxides of Other Elements

In many cases where the temperatures required for reaction of the halide MX_{2n} with the oxide MO_n are too high to yield the oxide halide, a foreign oxide M'O_m can be successfully used. This method has the disadvantage that it is often difficult to separate the foreign halide M'X_{2m} which is also formed [54,55]. Suitable sources of oxygen are oxides yielding halides M'X_{2m} which volatilize readily or which dissolve readily in inert solvents. On the other hand, the reaction can also be used in cases where a readily volatile or readily soluble oxide halide MO_{n-x}X_{2x} is formed. Finally, when this method is used for the preparation of oxide halides of intermediate valence states, redox reactions can sometimes be carried out simultaneously. The wide variety of possible sources of oxygen make this reaction appear extremely susceptible to development; the example of VOCl [56,57] was described as early as 1911 [Equation (g)], but has only very recently become prominent again.



[33] H. Schäfer, *Angew. Chem.* 73, 11 (1961); H. Schäfer: *Chemische Transportreaktionen*. Verlag Chemie, Weinheim/Bergstr. 1962.

[34] F. Hund, *Z. anorg. allg. Chem.* 265, 62 (1951).

[35] W. Klemm and H. A. Klein, *Z. anorg. allg. Chem.* 248, 167 (1941).

[36] W. Finkelburg and A. Stein, *J. chem. Physics* 18, 1296 (1950).

[37] W. H. Zachariasen, *Acta crystallogr.* 4, 231 (1951).

[38] B. B. Cunningham, D. C. Feay, and M. A. Rollier, *J. Amer. chem. Soc.* 76, 3361 (1954).

[39] H. Schäfer and E. Sibbing, *Z. anorg. allg. Chem.* 305, 341 (1960).

[40] K. Dehnicke, *Angew. Chem.* 73, 535 (1961).

[41] H. Schäfer and F. Kahlenberg, *Z. anorg. allg. Chem.* 305, 327 (1960).

[42] H. Schäfer, E. Sibbing, and R. Gerken, *Z. anorg. allg. Chem.* 307, 163 (1961).

[43] H. Schäfer, F. Wartenpfehl, and E. Weise, *Z. anorg. allg. Chem.* 295, 268 (1958).

[44] H. Schäfer and F. Wartenpfehl, *J. less-common Metals* 3, 29 (1961).

[45] H. Schäfer and F. Wartenpfehl, *Z. anorg. allg. Chem.* 308, 282 (1961).

[46] P. Ehrlich and H.-J. Seifert, *Z. anorg. allg. Chem.* 301, 282 (1959).

[47] A. Brukl and K. Ziegler, *Ber. dtsch. chem. Ges.* 65, 916 (1932).

[48] P. Baumgarten and W. Bruns, *Ber. dtsch. chem. Ges.* 72, 1753 (1939).

[49] J. Goubeau and H. Keller, *Z. anorg. allg. Chem.* 267,1 (1951).

[50] E. Thilo and P. Flögel, *Angew. Chem.* 69, 754 (1957); *Z. anorg. allg. Chem.* 329, 244 (1964).

[51] H. D. Fisher, W. J. Lehmann, and I. Shapiro, *J. physic. Chem.* 65, 1166 (1961).

[52] P. Hagenmüller, J. Rouxel, and B. LeNeindre, *C. R. hebd. Séances Acad. Sci.* 252, 282 (1961).

[53] H. Hahn and H. Katscher, *Z. anorg. allg. Chem.* 321, 85 (1963).

[54] P. Ehrlich and W. Engel, *Naturwissenschaften* 48, 716 (1961).

[55] P. Ehrlich and W. Engel, *Z. anorg. allg. Chem.* 317, 21 (1962).

[56] O. Ruff and H. Lickfett, *Ber. dtsch. chem. Ges.* 44, 506 (1911).

[57] F. Wedekind and C. Horst, *Ber. dtsch. chem. Ges.* 45, 262 (1912).

This method has recently been used to prepare new oxide halides, and has also been used as a simplified method of preparing oxide halides which are already known.

As₂O₃, Sb₂O₅, Bi₂O₃, and SiO₂ are found to be particularly suitable as sources of oxygen, as are TiO₂, CrO₃, NO₂, and SO₃. Thus pure TiOCl₂ is obtained very readily by the dissolution of As₂O₃ in TiCl₄ [54, 55], while CrOCl can be prepared from Bi₂O₃ or TiO₂ and CrCl₃ at a somewhat higher temperature [45]. The preparation of TaOCl₂, described above [42], can be modified in such a way that the oxygen is supplied by the quartz wall of the reaction vessel in the reaction of TaCl₅ with Ta. Oxide halides of elements of the main groups have also been prepared: *e.g.* AlOCl [58] from AlCl₃ and Sb₂O₅, and AlOI [59] from AlI₃, preferably with As₂O₃. SOF₄ [61], which is of interest on account of its versatility as a reactant [60], can be obtained from SF₄ by the use of vigorous oxidizing agents such as CeO₂ or CrO₃. The oxidation can also be carried out with NO₂ at 200 °C, or with catalytic quantities of NO₂ using atmospheric oxygen as the oxidizing agent.

V. Preparation of Oxide Halides by Thermal Degradation

The preparation of oxide halides by thermal degradation is subject to two conditions. On the one hand, decomposition must proceed at temperatures at which the resulting oxide halide is stable. On the other hand, the products must be easily separated and should therefore exhibit, for example, wide differences in their volatilities or solubilities.

Some oxide halides are obtainable by thermal degradation of other oxide halides. Thus, the I₂ vapor pressure over NbOI₃ reaches 1 atm at 270 °C, and NbOI₂ [62] is formed, while TiOI₂ loses iodine at 120 °C in vacuo, with formation of TiOI [63]. When NbOCl₃ is heated in a sealed tube, Nb₃O₇Cl is formed together with NbO₂Cl [64]. Thermal treatment of the bismuth oxide halides also yields compounds of complicated composition. For example, when heated to 700 °C BiOCl gives Bi₂₄O₃₁Cl₁₀ [65, 66]; the unusual ratios of the atoms in the latter can be explained from the sequence of the layers in the lattice [66], and this also accounts for its high thermal stability.

Other starting materials for the preparation of oxide halides by thermal degradation are strontium and barium fluorosulfonates which give good yields of sulfuryl fluoride at 500 °C, in accordance with Equation (h) [67].



[58] H. Schäfer, F. E. Wittig, and W. Wilborn, *Z. anorg. allg. Chem.* 297, 48 (1958).

[59] P. Hagemüller, J. Rouxel, J. David, and A. Colin, *Z. anorg. allg. Chem.* 323, 1 (1963).

[60] F. Seel and G. Simon, *Angew. Chem.* 72, 709 (1960).

[61] W. C. Smith and V. A. Engelhardt, *J. Amer. chem. Soc.* 82, 3838 (1960).

[62] H. Schäfer and R. Gerken, *Z. anorg. allg. Chem.* 317, 105 (1962).

[63] K. Dehnicke, *Angew. Chem.* 76, 578 (1964); *Angew. Chem. internat. Edit.* 3, 646 (1964).

[64] K. Huber and J. Baunok, *Chimia* 15, 365 (1961).

[65] A. E. Arppe, *Poggendorfs Ann. Physik Chem.* 64, 246 (1845).

[66] L. G. Sillen and M. Edstrand, *Z. Kristallogr., Mineralog. Petrogr. Abt.* 104, 178 (1942).

[67] E. L. Muetterties and D. D. Coffman, *J. Amer. chem. Soc.* 80, 5914 (1958).

VI. Preparation of Oxide Halides by Partial Halogenation of Oxides

Just as it is possible to replace part of the halogen in halides by oxygen, using an oxygen donor, oxides can be reacted with halogen donors. The particular problems of this method are very similar to those described in Sections III and IV. It has been found that halides which react to give readily volatile by-products are particularly suitable, *e.g.* BF₃, COCl₂, CCl₄, HF, HCl, HBr, F₂, Cl₂, certain interhalogen compounds, and, very recently, SeF₄.

On the other hand, it is also possible to use halides which do not give volatile reaction products if the resulting oxide halide itself is volatile or dissolves without decomposition. Of this group, particular mention should be made of HOSO₂F, SbF₃, AgF, KF, and CaF₂.

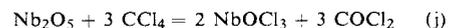
1. Chlorination with SOCl₂

Thionyl chloride has for some time been found to be a particularly easily manipulated reagent for the preparation of oxide chlorides. Thus VOCl₃ [68] can be prepared by simply heating V₂O₅ under reflux with the stoichiometric quantity of thionyl chloride. For the preparation of NbOCl₃ [69, 70] and WOCl₄ [69], on the other hand, the reaction must be carried out under pressure. However, the oxide chlorides are formed in a very pure state and in practically quantitative yield when the sulfur dioxide formed according to Equation (i) is removed.



2. Halogenation with CCl₄ and CBr₄

Some oxides can be partially halogenated with halides of carbon, generally at about 200 °C and therefore under pressure, with good results. To prevent complete halogenation of the oxide, stoichiometric quantities of the reactants are used. The carbon-halogen compounds must be free from carbon-hydrogen compounds, since reduction can otherwise occur. The reaction proceeds with formation of the readily volatile phosgene, *e.g.* according to Equation (j), and is particularly suitable



for the preparation of NbOCl₃ [71], NbOBr₃ [72], and WOCl₄ [73]. The tungsten oxide bromides WObBr₄ and WO₂Br₂ [74] can be prepared by varying the quantity of CBr₄ used.

[68] H. Hecht, G. Jander, and H. Schlapmann, *Z. anorg. allg. Chem.* 254, 255 (1947).

[69] H. Hecht, G. Jander, and H. Schlapmann, *Z. anorg. allg. Chem.* 254, 260 (1947).

[70] H. Hecht, G. Jander, and H. Schlapmann, *Z. anorg. allg. Chem.* 267, 213 (1952).

[71] D. E. Sands, A. Zalkin, and R. F. Elson, *Acta crystallogr.* 12, 21 (1959).

[72] M. Chaigneau, *C. R. hebd. Séances Acad. Sci.* 248, 3173 (1959).

[73] A. Michael and A. Murphy, *J. Amer. chem. Soc.* 44, 382 (1910).

[74] M. Pouraud and M. Chaigneau, *C. R. hebd. Séances Acad. Sci.* 249, 2568 (1959).

3. Halogenation with Halogens and Interhalogen Compounds

Among the halogens, only fluorine and interhalogen compounds containing fluorine can replace oxygen in oxides, owing to the electronegativity relationships. The replacement of bromine and iodine in oxide bromides and oxide iodides by chlorine and bromine, respectively, is of little interest, since it is easier in most cases to prepare the oxide chlorides directly. On the other hand, the replacement of chlorine in oxide chlorides by elementary fluorine is desirable in certain cases. The following may be used as fluorinating agents: F_2 , ClF_3 , BrF_3 , IF_3 , and IF_5 .

The reaction proceeds more readily with the polar interhalogen compounds than with fluorine, and consequently lower temperatures can be used in the former case. Thus a temperature of $475^\circ C$ is required for the preparation of VOF_3 [75] from V_2O_5 and F_2 , and even higher temperatures for the fluorination of MoO_3 with F_2 . On the other hand, reactions with interhalogen compounds always proceed at lower temperatures; OsO_3F_2 [76] can be very easily obtained from OsO_4 and BrF_3 . IF_3 and IF_5 are also occasionally used for the partial fluorination of oxides. CrO_3 and IF_3 react smoothly to give CrO_2F_2 [77], while IF_5 can be used to prepare MnO_3F from $KMnO_4$; similarly, $KReO_3$ reacts with IF_5 to yield ReO_3F [78]. VOF_3 [79] is very easily obtained by fluorination of $VOCl_3$ with ClF_3 ; this reaction proceeds even at room temperature.

4. Fluorination with SF_4 and SeF_4

It has been found very recently that SF_4 and SeF_4 are particularly effective fluorinating agents in some cases. Their reaction products SOF_2 and $SeOF_2$ are highly volatile, and can, therefore, be easily removed.

The excellent fluorinating properties of SF_4 and SeF_4 are essentially due to their structure: they form trigonal bipyramids in which two fluorine atoms and the lone pair of electrons are arranged equatorially, and the remaining two fluorine atoms occupy the apices [80, 81]. The compounds are thus structurally similar to the interhalogen compounds which are known to be good fluorinating agents, and to certain fluoride chlorides of group V elements, e.g. SbF_3Cl_2 which also forms a trigonal bipyramid [82]. Such structural similarities are reflected in the chemistry of these compounds. Thus CrO_3 can be fluorinated to CrO_2F_2 [83] at $5^\circ C$ using SF_4 . Also SeF_4 reacts very satisfactorily with CrO_3 or, more simply, with $K_2Cr_2O_7$, to form CrO_2F_2 [84, 85].

[75] L. E. Trevorrow, *J. phys. Chem.* 62, 362 (1958).

[76] M. A. Hepworth and P. L. Robinson, *J. inorg. nuclear Chem.* 4, 274 (1957).

[77] G. D. Flesch and H. J. Svec, *J. Amer. chem. Soc.* 80, 3189 (1958).

[78] E. E. Aynsley and M. L. Hair, *J. chem. Soc. (London)* 1958, 3747.

[79] K. Dehnicke and M. Afify, unpublished work.

[80] F. A. Cotton, J. W. George, and J. S. Waugh, *J. chem. Physics* 28, 994 (1958).

[81] J. A. Rolfe, L. A. Woodward, and D. A. Long, *Trans. Faraday Soc.* 49, 1388 (1953).

[82] K. Dehnicke and J. Weidlein, *Z. anorg. allg. Chem.* 323, 267 (1963).

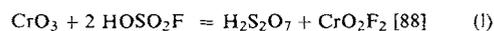
[83] H. L. Krauss and F. Schwarzbach, *Chem. Ber.* 94, 1205 (1961).

5. Halogenation with Hydrogen Halides and Halogenosulfonic Acids

In the reaction of hydrogen halides with oxides, the former are used in large excess; the reaction is carried out in the flowing gas to remove the water which is formed in accordance with Equation (k). For example,



the oxide chlorides of the rare earths, $MOCl$, can be prepared by passing a current of moist HCl over the sesquioxides M_2O_3 at high temperatures [86]; this reaction can also be used for the preparation of $AmOCl$ [87]. When halogenosulfonic acids are used as the halogenating agents, pyrosulfuric acid or alkali metal hydrogen sulfate is formed as a by-product [see Equations (l) and (m)].



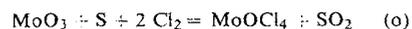
It is necessary, for the separation of the products, that halogenation should yield a readily volatile oxide halide. In this way NO_2Cl [90, 91] can be prepared under very mild conditions at $-60^\circ C$ from chlorosulfonic acid and HNO_3 .

6. Special Halogenating Agents

In this section we shall mention a few less important halogenating agents which have, nevertheless, made possible the synthesis of certain oxide halides. This group includes acetyl bromide which reacts with CrO_3 , as shown in Equation (n), and S_2Cl_2 which is the active



reagent for the chlorination of MoO_3 /sulfur mixtures to give $MoOCl_4$ [93] [Equation (o)].



Finally, BF_3 [94, 95], VF_5 [96] and CoF_3 [97] are also occasionally suggested as fluorinating agents for oxides.

[84] N. V. Sidgwick: *The Chemical Elements and their Compounds*. Clarendon Press, Oxford 1950, pp. 718, 1044.

[85] P. L. Robinson and N. Bartlett, *J. chem. Soc. (London)* 1961, 3549.

[86] C. W. Koch and R. J. Borg, cited by D. H. Templeton and C. H. Dauben, *J. Amer. chem. Soc.* 75, 6069 (1953).

[87] C. W. Koch, cited by D. H. Templeton and C. H. Dauben, *J. Amer. chem. Soc.* 75, 4560 (1953).

[88] H. v. Wartenberg, *Z. anorg. allg. Chem.* 247, 135 (1941).

[89] A. Engelbrecht and A. v. Grosse, *J. Amer. chem. Soc.* 76, 2042 (1954).

[90] M. Schmeisser, *Z. anorg. allg. Chem.* 255, 33 (1948).

[91] F. Seel and I. Nogrady, *Z. anorg. allg. Chem.* 269, 188 (1952).

[92] H. L. Krauss and K. Stark, *Z. Naturforsch.* 17b, 1 (1962).

[93] I. A. Glukhov and L. A. Tikhomirow, *Dokl. Akad. Nauk U.S.S.R.* 3, No. 2, 19 (1960); *Chem. Abstr.* 56, 9690 (1962).

[94] H. A. Lehmann and L. Kolditz, *Z. anorg. allg. Chem.* 272, 73 (1953).

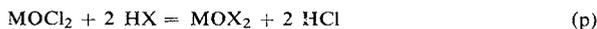
[95] A. Simon and R. Lehmann, *Z. anorg. allg. Chem.* 311, 224 (1961).

[96] H. C. Clark and H. J. Emel us, *J. chem. Soc. (London)* 1958, 192.

[97] O. Ruff and H. Lickfett, *Ber. dtsh. chem. Ges.* 44, 2539 (1911).

VII. Transhalogenation of Oxide Halides

The most important transhalogenating agents are HBr and HF which are reacted with oxide chlorides [Equation (p)]. The reactions generally proceed to completion,



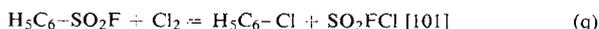
since the HCl formed is more volatile than HF and HBr. In this way, it is possible to prepare VOF₂ [97] from VOBBr₂, ReO₃F [89] from ReO₃Cl, or SeOBr₂ [98] from SeOCl₂.

Use is also made of the insolubility or the volatility of one of the reactants in the transhalogenation of oxide halides using other halogenating agents. Thus, SOCl₂ reacts very readily in liquid SO₂, with KBr dissolved in the latter, to yield SOBr₂ [99] which is deposited as a white precipitate. The volatility of SeOF₂ is utilized in the fluorination of SeOCl₂ by heating with KF [100]. In some cases, SbF₃ has also been found to be a good fluorinating agent for oxide chlorides, if a little SbCl₅ is added as a catalyst. Fluoride chlorides of Sb⁵⁺, the particular fluorinating properties of which have already been mentioned, presumably occur as intermediates. In this way, high yields of COF₂ [101] can be prepared from COCl₂ in an autoclave.

VIII. Oxide Halides with Two Halogen Components

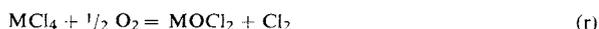
A number of oxide fluorochlorides can be prepared by reacting oxide chlorides with the theoretical amount of a fluorinating agent. Thus, SbF₃ is also suitable for partial fluorination of COCl₂ to give COFCl [101], or of SOCl₂ to give SOFCl [101]. To prepare CrO₂FCl [102], the oxide fluoride is combined with the oxide chloride in the molar ratio of 1:1.

An original preparation of sulfonyl fluoride chloride, SO₂FCl, involves controlled chlorination of an organically substituted oxide fluoride, namely benzene-sulfonyl fluoride [see Equation (q)].



IX. Oxide Halides from Halides and Oxygen

Just as fluorine can be used to replace part of the oxygen in oxides, part of the chlorine and bromine in chlorides and bromides can be replaced by oxygen, as shown in Equation (r).



[98] G. Govaert and M. Hansens, *Natuurwetensch. Tijdschr.* 20, 77 (1938).

[99] M. J. Frazer and W. Geraard, *Chem. and Ind.* 1954, 280.

[100] R. Paetzold and K. Aurich, *Z. anorg. allg. Chem.* 315, 72 (1962).

[101] H. J. Emeléus and J. F. Wood, *J. chem. Soc. (London)* 1948 2183.

[102] A. Engelbrecht and A. v. Grosse, *J. Amer. chem. Soc.* 74, 5262 (1952).

The lower reactivity of oxygen as compared to fluorine is compensated to some extent by the greater reactivity of chlorides and bromides as compared to the oxides. Thus VOCl [46] can be obtained by heating VCl₃ in a stream of oxygen, and UO₂Cl₂ [103] is formed from UCl₄ and oxygen at 300 °C. In other cases this method suffers from disadvantages, the most obvious of which are the heterogeneity (solid/gaseous) and the difficulty of metering the oxygen supply.

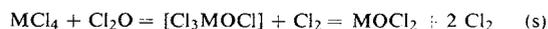
X. Oxide Halides by Oxidation of Lower Oxides or Oxide Halides with Halogens

This reaction, which has been known in principle for some time in the cases of NO and SO₂, was applied a few years ago to the preparation of ReO₃Cl [104] (from ReO₃ and chlorine at 160 °C) and ReO₂Br₂ [105] (from ReO₂ and Br₂).

The disadvantage of the low reactivity of many oxides can be avoided by reacting them, so the speak, in the nascent state with halides, *i.e.* by burning the element in gaseous halogen containing oxygen. In this way, for example, OsO₃F₂ [76] can be prepared from osmium in a current of O₂/F₂, or rhenium can be converted to ReOF₅ [106]. The required oxygen can also be formed in some cases by fluorination of the glass, as in the fluorination of ruthenium in a current of BrF₃/Br₂ to obtain RuOF₄ [107], or in the preparation of CrOF₄ [108] by direct fluorination of chromium. The method is still at a relatively early stage of its development and interesting variations are possible.

XI. Oxide Halides from Halides and Dichlorine Monoxide

The electropositive character of chlorine in dichlorine monoxide can be utilized for the preparation of oxide halides. Cl₂O reacts with many chlorides and bromides with partial replacement of chlorine or bromine by oxygen; hypochlorites occur as intermediates which cannot be isolated, and these spontaneously lose further halogen to form oxide chlorides [see Equation (s)].



This reaction was discovered as early as 1875, during a study of the properties of Cl₂O which reacted with PCl₅ to yield POCl₃ [109]; however, the reaction was not studied further until recently.

[103] H. A. Leary and J. F. Suttle in: *Inorganic Syntheses*. McGraw-Hill, New York-Toronto-London 1957, Vol. V, p. 148.

[104] C. J. Wolf, A. F. Clifford, and W. H. Johnston, *J. Amer. chem. Soc.* 79, 4257 (1957).

[105] R. Colton, *J. chem. Soc. (London)* 1962, 2078.

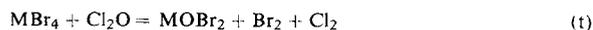
[106] E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *J. chem. Soc. (London)* 1950, 1622.

[107] J. H. Holloway and R. D. Peacock, *J. chem. Soc. (London)* 1963, 527.

[108] A. J. Edwards, *Proc. chem. Soc. (London)* 1963, 205.

[109] P. Spring, *Bull. Acad. Sci. Belgique* 2, 39, 895 (1875).

Oxide bromides can also be prepared by this method; however, when attempts are made to achieve higher yields, the chlorine liberated begins to form the oxide chloride. The reaction proceeds according to Equation (t).



Owing to the oxidizing action of Cl_2O and Cl_2 , only oxide chlorides in the highest valence states can be prepared by this method. The reactions proceed under very mild conditions at room temperature (and below), and, with the exception of the oxide bromides, are entirely free from side reactions. The only by-product formed is chlorine which can be easily removed. Cl_2O is very readily obtained by passing chlorine over mercuric oxide. It is not necessary to remove entrained chlorine, since this is formed as a by-product in any case; in the case of the oxide bromides, however, separation is recommended. The mildness of the conditions which can be achieved is shown particularly clearly in the case of $PbOCl_2$ [40, 109a] which is very sensitive to heat, and which is prepared from $PbCl_4$ and Cl_2O at $-10^\circ C$.

Thus it is possible, using the dichlorine monoxide method, to obtain thermally unstable oxide halides which cannot be prepared by commutation, and also oxide halides, the preparation of which (*e.g.* by partial hydrolysis of a halide) is subject to interference by by-products. Thus, it is also possible to prepare $SbOCl_3$ [110] and SbO_2Cl [111] from $SbCl_5$ and Cl_2O at room temperature, as well as VO_2Cl [112] from $VOCl_3$, $SnOCl_2$ [113] from $SnCl_4$, $TiOCl_2$ from $TiCl_4$ [113a], and AsO_2Cl [114] from $AsCl_3$.

The preparation of oxide chlorides is rather more difficult when it is necessary to use a solid chloride, *e.g.* $MoCl_5$, $TaCl_5$, or $ZrCl_4$, as the starting material. In this case, it may be helpful to add the theoretical amount of Cl_2O to a slurry of the chloride in CCl_4 cooled to $-30^\circ C$, and to warm slowly to room temperature with stirring. Good yields of $TaOCl_3$, $Ta_2O_3Cl_4$ [40], $ZrOCl_2$ [115], and $MoOCl_4$ [116] can be obtained in this way from the corresponding chlorides. The efficiency of the dichlorine monoxide method is shown especially clearly by the example of $ZrOCl_2$; all attempts to prepare this oxide chloride by other methods have failed.

The preparation of oxide bromides from metal bromides and Cl_2O can be achieved in the melt, using CCl_4 , however, in the case of $TiBr_4$ to yield $TiOBr_2$ [117]; similarly, $SnOBr_2$ [117] is obtained from $SnBr_4$.

Oxide fluorides can also be prepared, in some cases, with the aid of Cl_2O . The starting materials must be

definite fluoride chlorides, the chlorine of which is quantitatively replaced by the oxygen of Cl_2O , as shown in Equation (u). Thus $TiOF_2$ [118] is obtained by a



smooth reaction from TiF_2Cl_2 , while $SbOF_3$ [119] is formed from SbF_3Cl_2 , and SbO_2F [111] from $SbFCl_4$.

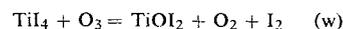
XII. Oxide Halides from Halides and Ozone

The reaction between certain halides and ozone is analogous to the reaction of oxide halides with chlorine monoxide. There is also some similarity between the structures of Cl_2O and O_3 : the bond angle is 116° in ozone, and is 109° in Cl_2O . Ozone is rather less reactive than dichlorine monoxide [*]. Thus $TiCl_4$, $SnCl_4$, and $VOCl_3$ react only at their boiling points, but yield extremely pure oxide chlorides $TiOCl_2$, $SnOCl_2$, and VO_2Cl [120]. The reactions proceed in accordance with Equation (v).



Apart from the exceptional purity of all products, the main advantage of this method over that using Cl_2O is the reaction of ozone with bromides at low temperatures to yield oxide bromides. Thus, $TiOBr_2$ can be obtained easily and very cheaply by passing a current of ozone, diluted with oxygen, into titanium bromide; $SnOBr_2$ is obtained from $SnBr_4$, and $VOBr_3$ reacts with ozone to yield the thermally unstable $V_4O_9Br_2$ [120].

Finally, it has very recently become possible to prepare oxide iodides by the ozone method. Since the metal iodides have relatively high melting points, so that reactions in the melt cannot be considered, it is necessary to use solvents for the reactions, which must be carried out as far as possible in the homogeneous phase; cyclohexane has proved to be a particularly useful solvent. Less soluble iodides are stirred up; as the dissolved iodide reacts with ozone, the supply is replenished from the solid. In this way it has been possible to prepare the oxide iodides $TiOI_2$, $SnOI_2$ [63], and $Ge_2O_3I_2$ [14]. A remarkable point about this reaction



[109a] K. Dehnicke, *Naturwissenschaften* 51, 535 (1964).

[110] K. Dehnicke, *Z. anorg. allg. Chem.* 312, 237 (1961).

[111] K. Dehnicke and J. Weidlein, unpublished work.

[112] K. Dehnicke in G. Brauer: *Handbuch der Präparativen Anorganischen Chemie*. F. Enke-Verlag, Stuttgart 1962, Vol 2, p. 1107.

[113] K. Dehnicke, *Z. anorg. allg. Chem.* 308, 72 (1961).

[113a] K. Dehnicke, *Z. anorg. allg. Chem.* 309, 266 (1961).

[114] K. Dehnicke, Lecture at the XVII. IUPAC Congress, München (Germany) 1959, No. A 1042.

[115] K. Dehnicke and K.-U. Meyer, *Z. anorg. allg. Chem.* 331, 121 (1964).

[116] L. Dorn, Ph. D. Thesis, Technische Hochschule Stuttgart, 1963.

[117] K. Dehnicke, *Angew. Chem.* 73, 763 (1961).

[118] K. Dehnicke, *Angew. Chem.* 74, 495 (1962).

[119] J. Weidlein, Diploma Thesis, Technische Hochschule Stuttgart, 1962.

[*] The reasons for the lower reactivity of O_3 towards MX_n as compared with that of Cl_2O may be the following: The greater bond angle of O_3 causes a decrease of donor properties of the central O-atom compared with that of Cl_2O . This renders more difficult the rate-determining primary step of adduct formation with the metal halides which act as Lewis acids. In addition, the polarity of the O-O bond of O_3 is less than that of the O-Cl bond in Cl_2O (cf. K. Dehnicke, *Chem. Ber.*, in the press).

[120] K. Dehnicke, *Angew. Chem.* 75, 419 (1963); *Angew. Chem. internat. Edit.* 2, 325 (1963).

(w) is that the iodine liberated does not react with the ozone to form iodine oxides until all the metal iodide has been consumed.

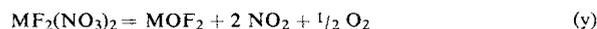
XIII. Preparation of Oxide Fluorides with the Aid of Chlorine Nitrate

A number of oxide fluorides cannot be prepared by the method using Cl_2O , owing to the low polarity of the M-Cl bonds in the fluoride chlorides which would be used, e.g. SnF_2Cl_2 . However, using the more strongly polar chlorine nitrate, ClONO_2 [121, 122], definite oxide fluorides can be obtained by an indirect route.

The products of the primary reaction [Equation (x)] are the fluoride nitrates [127] which can generally be isolated [*].



Chlorine nitrate is easily obtainable from N_2O_5 and Cl_2O [125] which are condensed in succession onto the fluoride chloride. In a second reaction step (y) the fluoride nitrate



[121] H. Martin and T. Jacobsen, *Angew. Chem.* 67, 524 (1955); *Z. physik. Chem. NF* 17, 375 (1958).

[122] M. Schmeißer, W. Fink, and K. Brändle, *Angew. Chem.* 69, 780 (1957).

[*] The reaction is possible owing to the pronounced electro-positive character of chlorine in chlorine nitrate [123, 124].

[123] K. Brändle, M. Schmeißer, and W. Lüttke, *Chem. Ber.* 93, 2300 (1960).

is thermally decomposed to form the corresponding oxide fluoride. This method is used for the preparation of AsOF_3 [126] from AsF_3Cl_2 , SbOF_3 [119] from SbF_3Cl_2 , SbO_2F [127] from SbCl_4F , SnOF_2 [118] from SnF_2Cl_2 , and Sn_2OF_6 [127] from SnFCl .

However, the fluoride chlorides required are only available in limited number and purity. It is, therefore, worth noting that lower fluorides also react with chlorine nitrate to yield the desired fluoride nitrates [see Equation (z)], the thermal decomposition of which



yields oxide fluorides, in accordance with Equation (y). Thus, the oxide fluorides SbOF_3 , SbO_2F , and TlOF [127] can be prepared in this way from SbF_3 , SbOF , and TlF , respectively.

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Translated by Express Translation Service, London

[124] A. J. Arvia, L. F. R. Cafferata, and H. J. Schumacher, *Chem. Ber.* 96, 1187 (1963).

[125] M. Schmeißer, W. Fink, and K. Brändle, cited by G. Brauer: *Handbuch der Präparativen Anorganischen Chemie*. F. Enke-Verlag, Stuttgart 1962, Vol. 1, p. 298.

[126] K. Dehnicke, *Angew. Chem.* 76, 385 (1964); *Angew. Chem. internat. Edit.* 3, 448 (1964).

[127] K. Dehnicke, J. Weidlein, and K. Krogmann, *Angew. Chem.* 75, 1110 (1963); *Angew. Chem. internat. Edit.* 3, 142 (1964).

Empirical Parameters of the Polarity of Solvents

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The empirical parameters of the polarity of solvents which have been determined recently are reviewed: Y-values (Winstein, Grunwald), X-values (Gielen, Nasielski), Ω -values (Berson, Hamlet, Mueller), Z-values (Kosower), E_T -values (Dimroth, Reichardt, Siepmann, Bohlmann), R- and S-values (Brownstein). Their field of application and interrelationships are discussed. The theoretical principles of the solvent effect on the reaction rate and light absorption of organic compounds are briefly described, and mention is made of attempts to correlate the physical characteristics of the solvent with the empirical parameters.

I. Introduction

The influence of solvents on the course of chemical reactions has long been known, but has only recently received sufficient attention as a result of the more detailed study of reaction mechanisms. As early as 1890, *Menschutkin* wrote that a reaction cannot be separated from the medium in which it takes place [1]. This raised

the problem of how the solvent affected the dissolved molecules, and the physical quantities by which this influence could be described in greater detail. *Menschutkin* postulated a relationship between the rate of reaction and the structure of the solvent. Most investigations were directed towards correlating the

[1] N. *Menschutkin*, *Z. physik. Chem.* 1, 611 (1887); 5, 589 (1890); 6, 41 (1890).