

ANODIC GENERATION OF POLYBROMOCHLORIDE IONS AND THEIR UTILIZATION AS PRECISELY-CONTROLLED OXIDIZING REAGENTS FOR EX-CELL INDIRECT ELECTROOXIDATION OF ALCOHOLS

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Abstract - Polybromo-chloride ions (Br_xCl_y^-) were generated by anodic oxidation of mixtures of Br^- and Cl^- in dichloromethane, and they could be used as precisely-controlled oxidizing reagents, of which oxidizing powers depended on the x - and y -values, for ex-cell indirect electrooxidation of a variety of alcohols.

Substrate molecules are reduced or oxidized by direct electron transfer on electrodes in ordinary (direct) electrolysis, while indirect electrolysis involves reactions of the substrates with reducing or oxidizing reagents generated by the direct electrolysis of their precursors. The indirect electrolysis is also classified into in-cell and ex-cell types. In the former, the reduction or oxidation of the substrates with the electrogenerated reagents takes place in the electrolytic cell, while in the latter the substrates react with the reagents in an auxiliary pot into which the electrolytic solutions containing the reagents are transported from the cell.

The indirect electrolysis can be a powerful technique, because it sometimes gives results quite different from those of the direct one. A variety of organic and inorganic, redox and non-redox, homogeneous and heterogeneous, and ionic and molecular reagents have been purposively used for indirect electroorganic synthesis.¹⁻³⁾

It is well known that anodic oxidation of halide ions provides a variety of positive/active halogen species which can effectively be used as oxidizing and/or halogenating reagents for organic compounds. The oxidation of halide ions (X^-) in aqueous media generates molecular halogens (X_2), trihalides (X_3^-), hypohalogenates (XO^-), halogenites (XO_2^-), halogenates (XO_3^-) and/or perhalogenates (XO_4^-). On the other hand, though the positive halogen species generated in non-aqueous media sometimes may be more useful as the reagents than those in aqueous ones, their chemical compositions and properties have been rarely studied. The species sometimes are collectively presented as $[\text{X}]^+$ or X^+ ,^{2,4)} because they have not been identified except for X_2 and X_3^- . Polyhalide ions (X_{2n+1}^-) and polyhalogen molecules (X_{2n}), some of which are known to be stable species,⁵⁻⁷⁾ may be possible species generated in non-aqueous media. Voltammetric and coulometric studies on anodic behavior of halide ions suggest the formation of X_3^- , X_5^- , X_2 , X_2^+ , X^+ and X^{3+} without any direct evidences.⁸⁻¹⁴⁾ Preparative electrolysis of I_2 in methanol also suggests the formation of a trivalent iodine species which is unlikely to be I^{3+} itself.¹⁵⁾

It is also well known that X_{2n} reacts easily with X^- to form X_{2n+1}^- and even in superacid systems X_{2n}^+ is slightly stable.¹⁶⁾ Becker and Zemach detected spectroscopically Br_3^- (269 nm) anodically-generated in acetonitrile.⁴⁾ From these considerations, the most likely positive halogen species anodically-generated in non-aqueous media may be X_{2n+1}^- (polyhalide ion). Discussions in this paper proceed on this basis.

In our previous work,¹⁷⁾ it was found that current efficiency for the in-cell indirect electrooxidation of benzyl alcohols and glycols with anodically-generated positive bromine reagents in dichloromethane decreased drastically with an increase in Br^- concentration at an equal amount of charge passed. This fact is not only important from a practical aspect of the indirect electrooxidation but also interesting from a mechanistic aspect. The fact was rationalized as due to the formation of Br_{2n+1}^- having different oxidizing powers with n -values. On the basis of cyclic-voltammetric and spectroscopic analyses of the anodic behavior of Br^- , it was tentatively concluded that (1) at amounts of charge less than $2/3 \text{ F mol}(\text{Br}^-)^{-1}$, Br_3^- (regarded as Br_{2n+1}^- at $n=1$) with the weakest oxidizing power is exclusively formed, (2) at amounts between $2/3$ and 1 F mol^{-1} , Br_{2n+1}^- ($n>1$) are formed and they have medium oxidizing powers: the Br_{2n+1}^- with the larger n -values formed at the larger amounts of charge have the stronger oxidizing powers, (3) at 1 F mol^{-1} the strongest Br_2 is formed and it is regarded as an ultimate Br_{2n+1}^- at $n=\infty$, and (4) at amounts larger than 1 F mol^{-1} , any clear UV-absorption can not be observed, probably, due to the formation of unstable bromine species which may be cationic ones.

In this work, polybromochloride ions (Br_xCl_y^-) anodically-generated from mixtures of Br^- and Cl^- in dichloromethane were electrochemically and spectroscopically investigated, and their reactivities were also examined in ex-cell indirect electrooxidation of alcohols.

Considerably large numbers of mixed polyhalides ($\text{Br}_x\text{Cl}_y\text{F}_z^-$) are known as their stable salts with a maximum of $v+x+y+z=9$.⁵⁻⁷⁾ A few (salts of Br_3^- , Br_2Cl^- , and BrCl_2^-) of them are commercially available and have sometimes been used as convenient reagents with well-controlled oxidizing and halogenating powers, though they are expensive. However, it is not easy to prepare them because of the inevitable use of hazardous molecular halogens or interhalogens under violent reaction conditions in most cases. In contrast, the anodic method may result in an easier generation of them under mild conditions. In this point of view, the anodic generation of mixed polyhalide ions should be worthy of being studied in detail.

Experimental

Typical experimental procedures are as follows: Current-potential curves were measured by a steady-state method on a Pt anode (2 x 3 cm) in 40 cm³ of 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ anolyte containing 50 mM Bu_4NBr at room temperature under a nitrogen atmosphere. The catholyte was also 22 cm³ of a 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ solution separated from the anolyte by glass frit diaphragm, and the cathode was a Pt plate (2 x 1.5 cm). Preparative electrolysis was also carried out galvanostatically at 8.3 mA cm⁻² of current density using a cell assembly similar to the above. After passing a certain amount of charge, an aliquot (0.1 cm³) of the anolyte was diluted with CH_2Cl_2 to be subjected to UV-spectroscopic analysis. An equimolar quantity of starting alcohols to the amount of charge passed was added to the anolyte and the resulting reaction mixture was allowed to stand for 18 h at 30°C, unless otherwise noted. Unreacted positive halogen reagents in the reaction mixture were quenched by shaking with a $\text{Na}_2\text{S}_2\text{O}_3$ solution, and the CH_2Cl_2 phase was dried over MgSO_4 and subjected to GC analysis of products.

Results and Discussion

Voltammetry: Figure 1 shows current-potential curves of Cl^- , Br^- and $\text{Cl}^- + \text{Br}^-$. Any additive property can not be observed in the current-potential curve of $\text{Cl}^- + \text{Br}^-$. It is also noted that the discharge potential of Br^- shifts positively in the presence of Cl^- which discharges at a much more positive potential. This fact

suggests an interaction between Cl^- and Br^- before or after the discharge of Br^- . For instance, it is likely that a mixed polyhalide (dibromochloride, Br_2Cl^-) ion is formed according to the following equations:

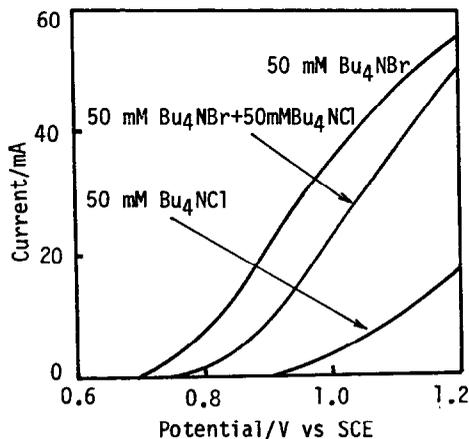
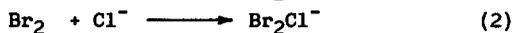
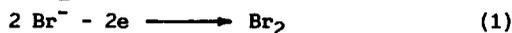


Fig. 1. Current-Potential Curves in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$

UV-Spectroscopy: It was found that λ_{max} of anodically-generated polybromide ions (Br_{2n+1}^-) in CH_2Cl_2 from Br^- in the absence of Cl^- was significantly affected by amounts of charge passed. As shown in Fig. 2, absorption bands were observed at 272 and 230 nm when amounts smaller than $2/3 \text{ F mol}^{-1}$ and of 1 F mol^{-1} were passed, respectively. The former and latter bands are attributed to Br_3^- and Br_2 .¹⁷⁾ At amounts between $2/3$ and 1 F mol^{-1} , Br_{2n+1}^- with different n -values may be formed.

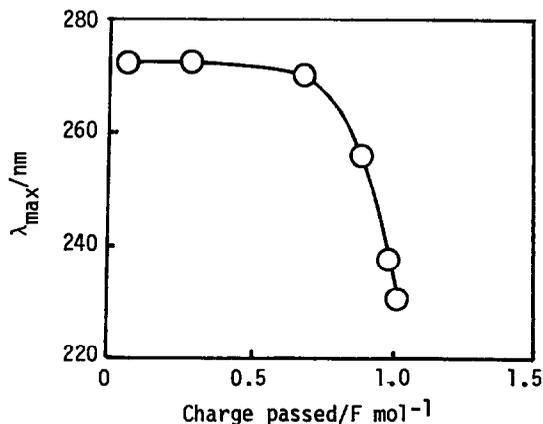


Fig. 2. Relation of λ_{max} of Br_{2n+1}^- to Amounts of Charge Passed in 50 mM Bu_4NBr

The absorption band of positive halogen species anodically-generated in a mixed system of $\text{Br}^- + \text{Cl}^-/\text{acetonitrile}$ was observed at 269 nm independent of the amounts of charge passed smaller than 2 F

$\text{mol}(\text{Br}^-)^{-1}$.⁴⁾ This fact indicates that only Br_3^- can be formed in acetonitrile regardless of the amounts of charge.

On the other hand, λ_{max} of the anodically-generated mixed positive halogen species in CH_2Cl_2 varied drastically with the amounts of charge as shown in Fig. 3. The mixed species is speculated to be Br_xCl_y^- ($x+y=\text{odd numbers}$). A species (272 nm) formed at a small amount of charge ($< 0.5 \text{ F mol}^{-1}$) may be Br_3^- (272 nm), and one (242 nm) at a large amount (2 F mol^{-1}) may be BrCl_2^- . Commercially supplied Bu_4NBr_3 , $\text{Bu}_4\text{NBr}_2\text{Cl}$ and $\text{Bu}_4\text{NBrCl}_2$ have the bands at 272,¹⁸⁾ 262 and 242¹⁸⁾ nm, respectively.

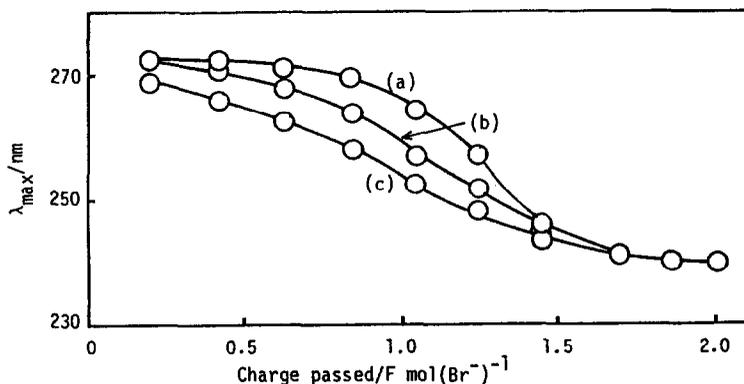
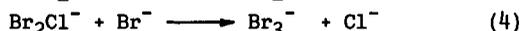
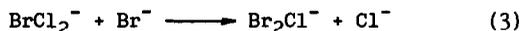


Fig. 3. Relation of λ_{max} of Br_xCl_y^- to Amounts of Charge Passed in $\text{Br}^- + \text{Cl}^-$ Mixed Systems: (a) 50 mM Bu_4NBr + 50 mM Bu_4NCl , (b) 50 mM Bu_4NBr + 150 mM Bu_4NCl , and 50 mM Bu_4NBr + 400 mM Bu_4NCl

Chemical preparation of Br_xCl_y^- : Generally it is not easy to prepare Br_xCl_y^- by chemical methods.¹⁹⁾ Some (Br_3^- and Br_2Cl^-) of them could be prepared by means of interconversion by the reaction with Br^- (Eqs. 3,4). However, the reaction with Cl^- did not occur even when excess amounts of Cl^- were used.



On the other hand, Br_2 and Br_3^- reacted with Cl^- to give products with λ_{max} [less than 262 nm (Br_2Cl^-) and 272 nm (Br_3^- itself), respectively] continuously changing with amounts of Cl^- added, but only 10 nm of variation in the λ_{max} could be observed even when more than a hundred equimolar Cl^- were added. Hence, compared to the chemical method, the anodic one is not only more convenient but also can provide Br_xCl_y^- with more widely variable λ_{max} . If the value of λ_{max} indicates the oxidizing power of Br_xCl_y^- reagents, the above fact should be practically important from an organic synthesis aspect.

Structure of Br_xCl_y^- : The highest known polyhalide ions may consist of 17 halogen atoms.^{5,7)} Although a number of studies have been made by means of vibrational²⁰⁻²²⁾ and electronic^{16,18,23)} spectroscopies, nuclear quadrupole coupling constant measurement^{24,25)} and conductometry,²⁶⁾ the structure of polyhalide ions has not been made completely clear. A reasonable structure between cationic, anionic and atomic halogens was postulated for polyhalide ions consisting of 3 and 5 halogen atoms.^{24,25)} In this situation, it seems to be difficult to specify the structure of anodically-generated Br_xCl_y^- . Therefore, the oxidizing capacity and power of Br_xCl_y^- , which seem to be directly related to the values of x and y , will be discussed in detail below.

Oxidizing capacity of Br_xCl_y^- : It was confirmed by iodometry that the total oxidizing capacity of an anodic solution after electrolysis was proportional to the amount of charge passed, regardless of the Cl^-/Br^- ratio in the original anodic solution. In addition, the commercially available Bu_4N^+ salts of Br_3^- , Br_2Cl^- and BrCl_2^- had an equal oxidizing capacity equivalent to an imaginary Br^+ . From these facts and Fig. 3, it may be suggested that the oxidizing capacity of Br_xCl_y^- is equivalent to $1/2(x+y)\text{Br}^+$, and the product of $1/2(x+y)$ and amount of Br_xCl_y^- formed is proportional to the amount of charge passed.

Oxidizing power of Br_xCl_y^- : Positive halogen species are well known as convenient oxidizing reagents for oxidation of alcohols to the corresponding carbonyl compounds. Oxidizing powers of the same type of the reagents consisting of different halogens are generally ordered as $\text{Cl} > \text{Br} > \text{I}$.²⁷⁾ In this work, the oxidizing power of Br_xCl_y^- was examined in the oxidation of alcohols as a test reaction.

The oxidation was carried out by means of ex-cell indirect electrolysis in which 1 mole of the alcohols per 2 F of charge passed were reacted. Therefore, the yield of the carbonyl compounds formed should be a relative indication for the oxidizing power of Br_xCl_y^- anodically-generated at different amounts of charge passed.

As shown in Fig. 4, the yield of benzaldehydes in the oxidation of benzyl alcohols was significantly increased with an increase in the amount of charge passed, while product-selectivity for the benzaldehydes

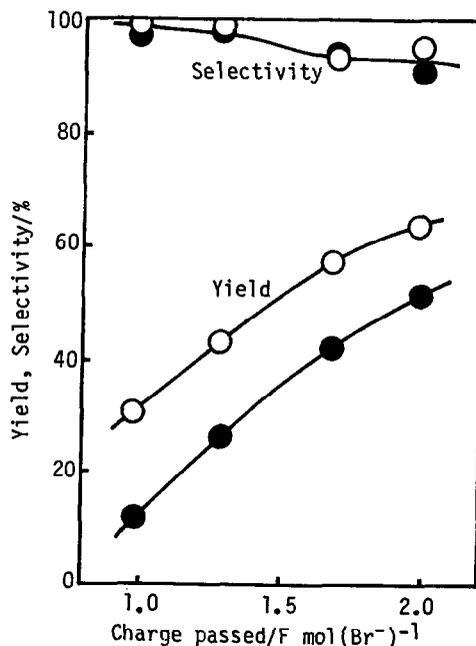


Fig. 4. Yield and Selectivity for Benzaldehydes in the Oxidation of Benzyl Alcohols(-●- ; Benzyl Alcohol and -○- ; p-Methylbenzyl Alcohol with Anodically-Generated Br_xCl_y^- at $\text{Cl}^-/\text{Br}^- = 1$

was slightly decreased with an increase in the charge. The former fact indicates that a Br_xCl_y^- generated at a larger amount of charge has a stronger oxidizing power. In other words, a Br_xCl_y^- with a smaller λ_{max} or a larger y/x ratio has a stronger oxidizing power which results in a higher yield and a lower product-selectivity.

Addition of 2,6-lutidine as a base had no influence on the oxidizing power of Br_xCl_y^- , while the dependence of the oxidizing power on the amount of charge passed disappeared in the presence of K_2CO_3 . No significant influence of the concentration of Br_xCl_y^- was observed. As expected from Fig. 3, the initial ratio of Cl^-/Br^- in the anodic solution was also an important controlling factor of the oxidizing power as well as the amount of charge.

As shown in Fig. 5, a similar dependence of the oxidizing power on the amount of charge was also observed in the oxidation of DL- α -phenethyl alcohol and 2-methylcyclohexanol in the presence of 2,6-lutidine which was used to prevent the α -bromination of ketones formed.

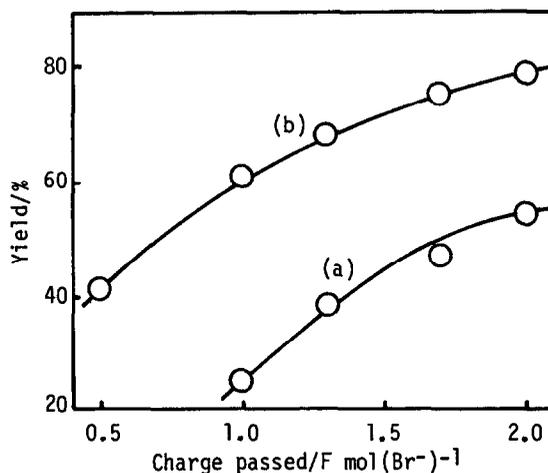


Fig. 5. Yield of Ketones in the Oxidation of (a) DL- α -Phenethylalcohol and (b) 2-Methylcyclohexanol

Substrate-selectivity control: It was found that substrate-selectivity in the oxidation of mixed starting substrates was effectively controlled by controlling the amount of charge passed for generating Br_xCl_y^- . As shown in Fig. 6, the higher selectivities were obtained using Br_xCl_y^- with weaker oxidizing powers generated at the smaller amounts of charge.

Product-selectivity control: The oxidation of meso-hydrobenzoin gives a mixture of benzil and benzoin in general. As shown in Fig. 7, not only their total yields but also selectivities were drastically varied with the amount of charge passed for generating Br_xCl_y^- . This fact indicates that anodically-generated Br_xCl_y^- can be used as reagents for product-selectivity controlled oxidation.

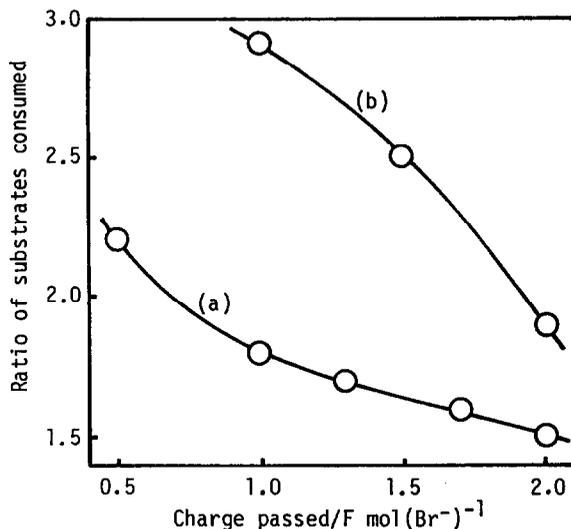


Fig. 6. Substrate-Selective Oxidation of 1:1 Mixtures of (a) Cis-/Trans-2-methylcyclohexanol and (b) DL- α -Phenethyl/Benzyl Alcohols

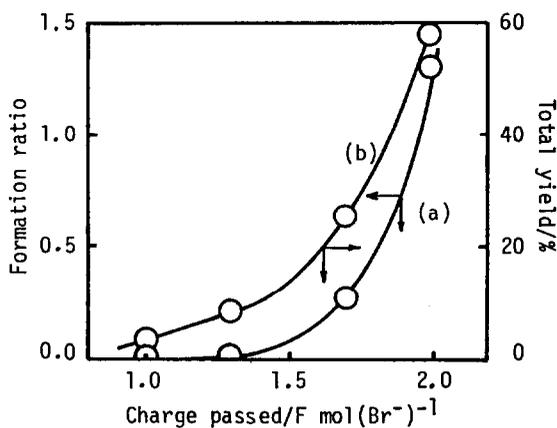


Fig. 7. Product-Selective Oxidation of meso-Hydrobenzoin: (a) Formation Ratio of Benzil/Benzoin and (b) Total Yield.

Conclusions

Anodic oxidation of mixtures of Br⁻ and Cl⁻ in CH₂Cl₂ provides mixed positive halogen species, which seem to be polybromochloride ions (Br_xCl_y⁺) and to have oxidizing powers precisely-controlled by the amount of charge passed for generating them. Therefore, they can be used for well-controlled oxidation of alcohols. Furthermore, they can be also used to control substrate- and product-selectivities in the oxidation.

In a further investigation in progress, it is being indicated that the polybromochloride ions can also be used as well-controlled brominating reagents for a variety of organic compounds.

References

1. Simonet, J. *Organic Electrochemistry, An Introduction and a Guide*, 2nd. Ed. by Baizer, M. M.; Lund, H., MerceL Dekker, New York(1983), p. 843.
2. Torii, S. *Electroorganic Synthesis, Methods and Applications*, Part 1, Kodansha-VCH, Tokyo(1985), p. 279.
3. Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd. Ed., Wiley, New York(1989), p. 290.
4. Becker, J. Y.; Zemach, D. J. *Chem. Soc. Perkin Trans. II*, 1981, 336.
5. Popov, A. I. *Halogen Chemistry*, Vol. 1, ed. by Gutmann, Academic Press, London(1967), p. 225.
6. Downs, A. J.; Adams, C. J. *The Chemistry of Chlorine, Bromine, Iodine and Astatine*, Pergamon Press, Oxford(1973), p. 1534.
7. Popov, A. I.; Buckles, R. E. *Inorganic Syntheses*, Vol. 5, ed. by Moeller, T., McGraw-Hill, New York(1957), p. 167.
8. Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* 1957, 79, 1852.
9. Adkani, G.; Herlem, M. J. *Electroanal. Chem.* 1970, 26, 363.
10. Sereno, L.; Macagno, V. A.; Giordano, M. C. *Electrochim. Acta*, 1972, 17, 561.
11. Popov, A. I.; Geske, D. H. *J. Am. Chem. Soc.* 1958, 80, 5346.
12. Popov, A. I.; Geske, D. H. *J. Am. Chem. Soc.* 1958, 80, 1340.
13. Feoktistov, L. G.; Andreev, G. V.; Tomilov, A. P. *Elektrokhim.* 1988, 24, 37.
14. Behl, W. K. *J. Electrochem. Soc.* 1989, 136, 2305.
15. Shono, T.; Samain, H. C.; Matsumura, Y. *12th Electroorganic Chemistry Symposium*, June 28-29, 1990, Hiroshima, Abstr. No. 29.
16. Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* 1972, 11, 586.
17. Takiguchi, T.; Nonaka, T. *Bull. Chem. Soc. Jpn.* 1987, 60, 3137.
18. Gabes, W.; Stufkens, D. J. *Spectrochim. Acta*, 1974, 30A, 1715.
19. Chattaway, F. D.; Hoyle, G. *J. Chem. Soc.* 1923, 123, 654.
20. Person, W. B.; Anderson, G. R.; Fordemwalt, J. N.; Stammreich, H.; Forneris, R. *J. Chem. Phys.* 1961, 35, 908.
21. Evans, J. C.; Lo, G. Y.-S. *J. Chem. Phys.* 1966, 40, 4356.
22. Evans, J. C.; Lo, G. Y.-S. *Inorg. Chem.* 1967, 6, 1483.
23. Buckles, R. E.; Mills, J. F. *J. Am. Chem. Soc.* 1954, 76, 4845.
24. Cornwell, C. D.; Yamasaki, R. S. *J. Chem. Phys.* 1957, 27, 1060.
25. Yamasaki, R. S.; Cornwell, C. D. *J. Chem. Phys.* 1959, 30, 1265.
26. Popov, A. I.; Deskim, W. A. *J. Am. Chem. Soc.* 1958, 80, 2976.
27. Katsumura, S.; Isoe, Y. *Shin-Zikkenkagaku-Koza, Sanka to Kangen*, Vol. 15, Part I-1, ed. by Chem. Soc. Jpn., Maruzen, Tokyo(1976), Chap. 8.