[April, 1992] *Bull. Chem. Soc. Jpn.,* ***65,*** *943—948 (1992)*

Anodically-Generated Br–Cl Composite Halogenating Reagents

Kouta Fukui and Tsutomu Nonaka*
Department of Electronic Chemistry, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227
(Received January 10, 1991)

The halogenating power of Br–Cl composite species (termed "BC-reagent" in this article) generated anodically from mixtures of Br^- and Cl^- in CH_2Cl_2 was examined in an ex-cell manner toward some organic compounds. The BC-reagent brominated methoxybenzenes, and the brominating power could be precisely controlled by means of the amount of electricity charged and by varying the ratio of Cl^-/Br^-. The power of the reagent was less controllable during the bromination of aniline. The reaction of olefins with the BC-reagent led to dibromination and bromochlorination, the product-selectivity of which could be also controlled. The theoretically calculated chemical composition of the BC-reagent agreed fairly well with the experimentally confirmed value in some cases.

In general, although chemical reactions can be arbitrarily controlled by suitably selecting the reagents and/or reaction conditions, it is difficult to control the reactivity of the reagents both widely and precisely. In a previous study,[1] we reported that Br–Cl composite species (termed "BC-reagents" in this article), which were most likely polybromochloride ions, ($Br_xCl_y^-$), were generated by anodic oxidation of mixtures of Br^- and Cl^- in CH_2Cl_2. The oxidizing ability of the reagent could be precisely controlled by varying the amount of charge passed and the ratio of Cl^-/Br^- for their generation. This BC-reagent was found to be useful for the oxidation of a variety of alcohols in an ex-cell manner.

In this work, the halogenating powers of the BC-reagents were examined by using methoxybenzenes (anisole (**1**) and 1,2-dimethoxybenzene (**4**)), aniline (**8**), and olefins (styrene (**12**) and cyclohexene (**15**)) as test compounds. These compounds are known to be brominated and/or bromochlorinated with positive bromine reagents such as Br_2,[2] BrCl,[3–6] NBS,[7] and the salts of trihalide ions (Br_3^-,[8–11] Br_2Cl^-[6] and $BrCl_2^-$[12–14]).

Results and Discussion

Bromination of Methoxybenzenes. An electrochemical stoichiometry for the substitutive halogenation of C–H to C–X with positive halogen species (conventionally, $[X]^+$[15–17]) anodically-generated from halide ion (X^-) can be formally represented by the following equations:

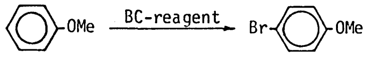
$$X^- \rightarrow [X]^+ + 2e \qquad (1)$$

and

$$\text{C–H} + [X]^+ \rightarrow \text{C–X} + H^+. \qquad (2)$$

Therefore, on the basis of this stoichiometry, the passage of 2F of charge is required to convert 1 mol of anisole (**1**) into 4-bromoanisole (**2**). Thus, 0.5 mol(**1**) F^{-1} corresponds to 1 equiv mol of **1**.

The starting compound **1** (1.0 equiv mol) was reacted in anolytes which originally contained 0.05 M (1 M=1 mol dm^{-3}) Br^- and 0.05 M Cl^- (Cl^-/Br^- ratio (r)=1) in CH_2Cl_2; they were electrolyzed by passing various amounts of charge for the generation of Br–Cl composite positive halogen species (BC-reagents). After a reaction for 24 h, the unreacted BC-reagents were decomposed with $Na_2S_2O_3$ and the reaction mixture was analyzed. Figure 1 shows the relationship between the yield of **2** and the amount of charge passed (Q/F mol(Br^-)$^{-1}$), based on the Br^- used. It is clear that the brominating power of the BC-reagent is greatly affected by Q. No by-product was detected and the material balance on the basis of the recovered **1** was always 100%.



(3)

1 **2**

Commercially available Bu_4NBr_2Cl and Bu_4NBrCl_2 reagents (0.05 M in CH_2Cl_2) reacted with 1 equiv mol of **1** under conditions similar to those given in Fig. 1 to give **2** in 33 and 58% yields, respectively. From these

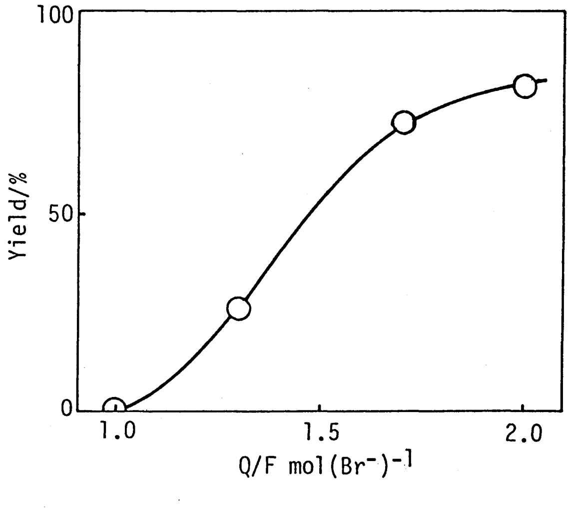


Fig. 1. Relationship between the yield of **2** and Q (amount of charge passed) in the bromination of **1** (1.0 equiv mol) with the BC-reagent generated in 0.05 M Et_4NBr+0.05 M Et_4NCl (r(Cl^-/Br^-)=1).

results, Br_2Cl^- and $BrCl_2^-$ can be regarded as having brominating powers equal to those of the BC-reagents generated at Q=1.34 and 1.54 F mol(Br^-)$^{-1}$, respectively (Fig. 1), if the influence of the concentration of the reagents on the yield is negligibly small. Figure 2 shows the results obtained for different concentrations of the BC-reagents generated in different concentrations of Br^- at $r(Cl^-/Br^-)=1$. From Fig. 2, it is confirmed that the brominating power of the BC-reagent is not influenced by the concentration. The above Q values are considerably smaller than the theoretical value (Q=2 F mol(Br^-)$^{-1}$) for the formation of Br_2Cl^-.

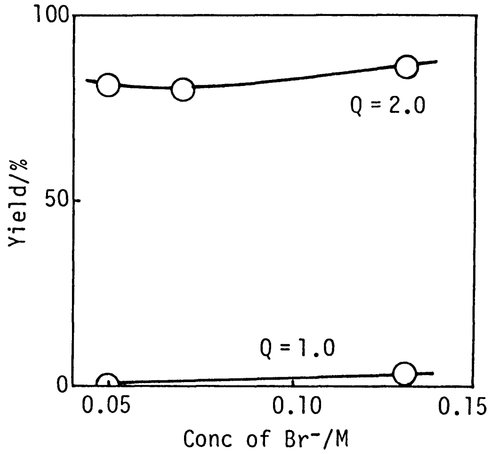


Fig. 2. Relationship between the yield of **2** and the concentration of Br^- ($r(Cl^-/Br^-)=1$) in the bromination of **1** (1.0 equiv mol) with the BC-reagent generated at Q (amount of charge passed)=1.0 and 2.0 F mol(Br^-)$^{-1}$.

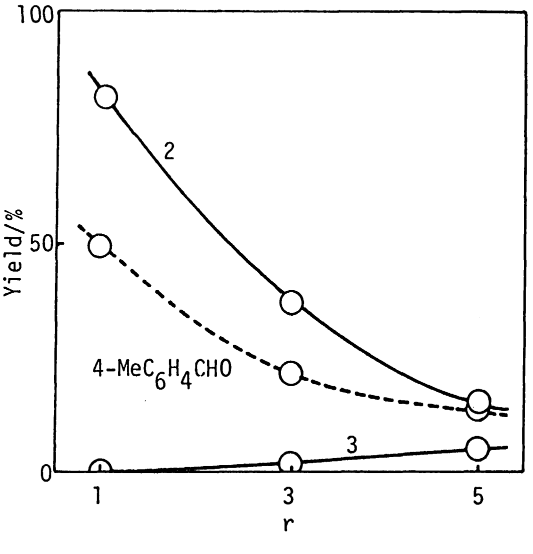
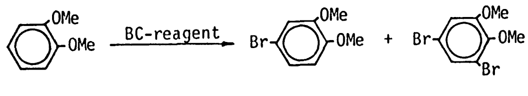


Fig. 3. Relationship between the yield and $r(Cl^-/Br^-)$ at Q (amount of charge passed)=2.0 F mol(Br^-)$^{-1}$. The concentration of Et_4NBr=0.05 M. The solid line indicates the bromination of **1** (1.0 equiv mol) with the BC-reagent, and the dotted line the oxidation of $4\text{-}MeC_6H_4CH_2OH$ (1.0 equiv mol).

Figure 3 shows the relationship between the yields and $r(Cl^-/Br^-)$ at Q=2 F mol(Br^-)$^{-1}$. The yield of **2** decreased significantly with an increase in r, and small amounts of 4-chloroanisole (**3**) were formed at large r's. These results apparently indicate that the BC-reagents bearing relatively weaker brominating and stronger chlorinating powers are generated at larger r. That is, the BC-reagents with positive chlorine components are generated; this was confirmed by a controlled experiment in which once **2** formed it was not converted into **3** by halogen exchange under the reaction conditions used. As described above, polybromochloride ions ($Br_xCl_y^-$) were supposed to be the most likely species constituting BC-reagents in our previous work.[1] However, it is unlikely that $Br_xCl_y^-$ ions with larger chlorine contents (relatively larger y-values) are generated at larger r, since this is obviously inconsistent with the above observed fact that the Bu_4NBrCl_2 reagent has a stronger brominating power than the Bu_4NBr_2Cl. Therefore, the possible generation of $Br_xCl_y^-$ ions may be excluded.

A similar influence of r on the oxidizing power of the BC-reagents was observed in the oxidation of 4-methylbenzyl alcohol to 4-methylbenzaldehyde (Fig. 3).

The bromination of 1,2-dimethoxybenzene (**4**) with the BC-reagents gave 4-bromo-1,2-dimethoxybenzene (**5**) and 4,6-dibromo-1,2-dimethoxybenzene (**6**) (Eq. 4).



4 **5** **6** (4)

As shown in Fig. 4, when 1 equiv mol of **4** was reacted, **5** was formed as the main product and small amounts of **6** were detected at large Q's. The material

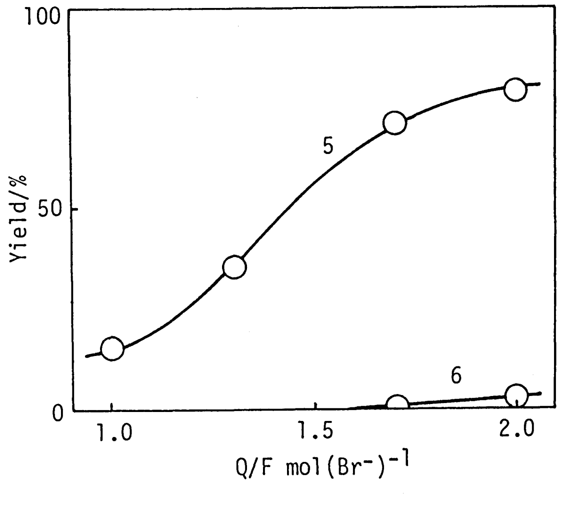


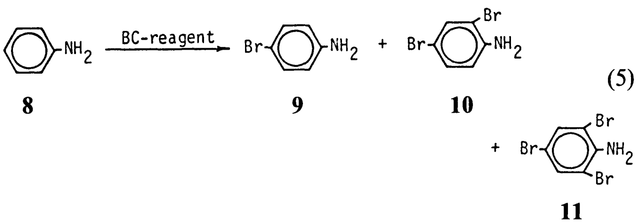
Fig. 4. Relationship between the yields of **5** and **6**, Q (amount of charge passed) in the bromination of **4** (1.0 equiv mol) with the BC-reagent generated in 0.05 M Et_4NBr+0.05 M Et_4NCl ($r(Cl^-/Br^-)=1$).

balance on the basis of the recovered **4** was in the range of 95—100%. The yields of the products increased with an increase in Q. The bromination of **4** with the Bu_4NBr_2Cl and Bu_4NBrCl_2 reagents indicated that they have brominating powers corresponding to the BC-reagents generated by passing Q=1.39 and 1.58 F mol(Br$^-$)$^{-1}$, respectively. These values are close to those obtained in the bromination of **1** (Fig. 1). Bu_4NBr_2Cl and Bu_4NBrCl_2 also gave small amounts, 2 and 4% yields, respectively, of 4-chloro-1,2-dimethoxybenzene (**7**). The brominating power of the Bu_4NBr_3 reagent was also estimated to correspond to that of the BC-reagent generated at Q=1.00 F mol(Br$^-$)$^{-1}$. However, this fact cannot be simply rationalized, since the theoretical Q for generating Br_3^- from Br^- is not 1, but 2/3 F mol(Br$^-$)$^{-1}$.

The Bu_4NBr_3, Bu_4NBr_2Cl, and Bu_4NBrCl_2 reagents exhibited UV absorption maxima (λ_{max}'s) at 273, 262, and 240 nm in CH_2Cl_2, respectively. In previous studies,[1] it was found that the λ_{max}'s of the BC-reagents decreased with an increase in Q. The Q's required for generating the BC-reagents having λ_{max}'s equal to those of the above three trihalide ion reagents are summarized in Table 1. The Q's estimated from the λ_{max}'s of Bu_4NBr_3 and Bu_4NBr_2Cl significantly decrease with an increase in r, while those from the λ_{max} of Bu_4NBrCl_2 increase slightly. Moreover, it should be noted that all of the Q's estimated from the λ_{max}'s are quite different from those estimated from the brominating powers.

A more complicated product distribution was observed upon using 0.5 equiv mol of **4**, as shown in Fig. 5. At Q<1.5 F mol(Br$^-$)$^{-1}$, **5** was formed as a sole product; the yield increased simply with an increase in Q, similarly to the trend shown in Fig. 4. The starting **4** was completely consumed at Q=ca. 1.5 F mol(Br$^-$)$^{-1}$. At Q>1.5 F mol(Br$^-$)$^{-1}$, mixtures of **5** and **6** were formed. These facts indicate that the bromination of **4** takes place stepwise and that the product distribution can be controlled by selecting Q. The total yield of **5** and **6** at Q>1.5 F mol(Br$^-$)$^{-1}$ was in the range 90—100%.

Bromination of Aniline. The bromination of aniline (**8**) was similarly examined in the presence of K_2CO_3 powder (Eq. 5). When 1 equiv mol of **8** was reacted with BC-reagents, 4-bromoaniline (**9**) and 2,4-dibromoaniline (**10**) were formed in ca. 60 and 20% yields, respectively, at any Q used, as shown in Fig. 6. 2,4,6-Tribromoaniline (**11**) was not detected. The bromination efficiency (yield of **9**+2× yield of **10**) was in the range 95—100% at all of the Q values used. Consequently, the BC-reagents used were almost completely consumed, while ca. 20% of the starting **8** always



(5)

Table 1. Amount of Charge (Q) Passed for the Generation of BC-Reagents Having UV Absorption Maxima (λ_{max}) Equal to Those of Commercially Available Trihalide Ion Reagents

Trihalide ion reagent (λ_{max} in CH_2Cl_2/nm)	Q/F mol (Br$^-$)$^{-1}$		
	r=1	r=3	r=8
Bu_4NBr_3 (273)	<0.6	<0.3	<0.1
Bu_4NBr_2Cl (262)	1.09	0.95	0.67
Bu_4NBrCl_2 (240)	1.90	1.97	2.00

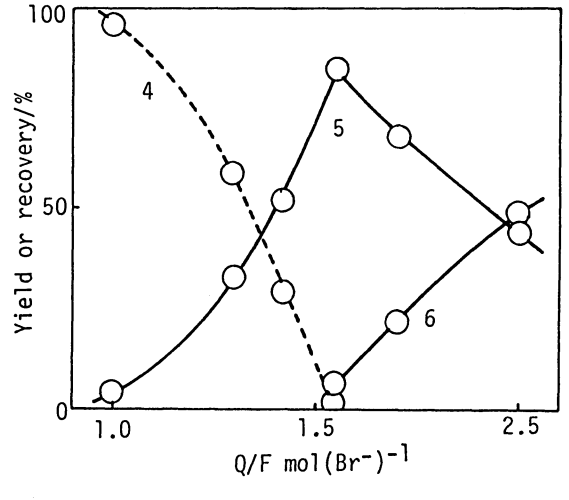


Fig. 5. Relationship between the yields of **5** and **6** and the recovery of unreacted **4**, and Q (amount of charge passed) in the bromination of **4** (0.5 equiv mol) with the BC-reagent generated in 0.05 M Et_4NBr+ 0.05 M Et_4NCl (r(Cl^-/Br^-)=1).

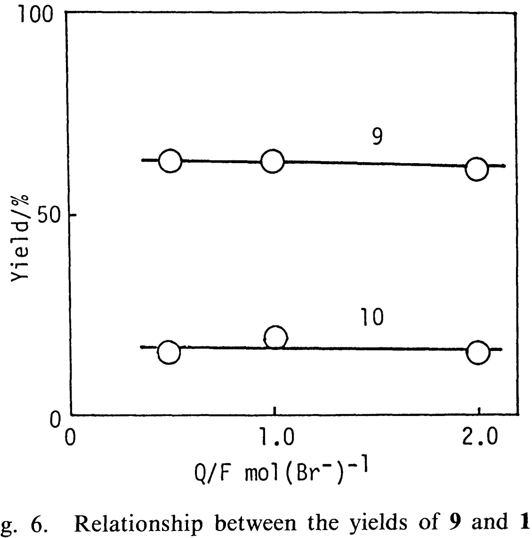


Fig. 6. Relationship between the yields of **9** and **10**, and Q (amount of charge passed) in the bromination of **8** (1.0 equiv mol) with the BC-reagent generated in 0.1 M Et_4NBr+0.1 M Et_4NCl (r(Cl^-/Br^-)=1).

remained unreacted. No influence of Q on the yield and efficiency may be rationalized as being due to the ease of bromination of not only **8**, but also **9**, under the reaction conditions used.

As shown in Fig. 7, the bromination of 0.5 equiv mol of **8** resulted in a product distribution pattern that is quite different from that for 0.5 equiv mol of **4** (See Fig. 5). It is reasonable that **10** was a main product, since a theoretical amount of the BC-reagents for the formation of **10** was used; no unreacted **8** was detected. The total yield and the bromination efficiency ((yield of **9**+2× yield of **10**+3× yield of **11**)×0.5) were also in a range of 95—100% for any Q. The yield of **10** decreased with an increase in Q, while that of **11** increased. This fact indicates that the bromination of **10** is not easy and, consequently, that it is more efficiently brominated with BC-reagents having stronger brominating powers at larger Q's. However, a slight increase in the yield of **9** cannot be rationalized in this way.

As described above, **8** exhibited different features in the bromination from those of **1** and **4**. Positive halogen species interact strongly with organic nitrogen compounds such as nitriles, amides and pyridines to sometimes form stable adduct complexes.[18] Some of the different features may be caused by an interaction of the BC-reagents with the amino group of **8**, itself.

Dibromination and Bromochlorination of Olefins.

An electrochemical stoichiometry for the electrophilic halogenation of olefins is formally represented in Eqs. 1 and 6.[19] Thus, 0.5 mol(olefin) F^{-1} corresponds to 1 equiv mol of olefin.

$$\mathrm{C{=}C} + [\mathrm{X}]^+ + \mathrm{X}^- \rightarrow \mathrm{X{-}C{-}C{-}X} \qquad (6)$$

Excess amounts (>1.5 equiv mol) of olefins, such as styrene(**12**) and cyclohexene (**15**), were reacted with the BC-reagents in an olefin concentration equal to the original one of Br^- give mixtures of the corresponding dibrominated and bromochlorinated products. The total halogenation efficiency was not affected by the kind and amount of these olefins or by Q, and was in the range 97—100%. Material balances, based on the recovered olefins, were also in the 95—100% range. These facts suggest that the halogenating power of the BC-reagents in olefin halogenation should be interesting from a point of view not shown in the methoxybenzene and aniline brominations; consequently, attention was turned to the effect of Q and r on the product-selectivity of bromochlorinated/dibrominated products.

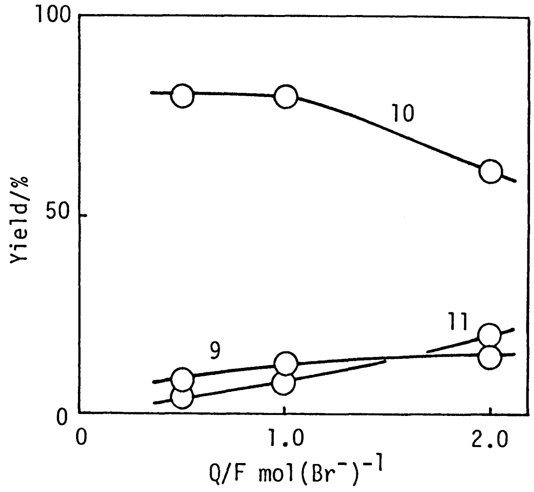


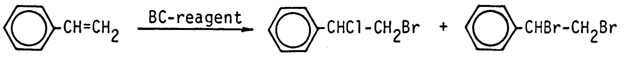
Fig. 7. Relationship between the yields of **9**—**11** and Q (amount of charge passed) in the bromination of **8** (0.5 equiv mol) with the BC-reagent generated in 0.1 M $\mathrm{Et_4NBr}$+0.1 M $\mathrm{Et_4NCl}$ ($r(\mathrm{Cl^-/Br^-})=1$).

When values of $Q<2$ $\mathrm{F\,mol(Br^-)^{-1}}$ were used in this study, it was likely that Br^- was exclusively oxidized to $[\mathrm{Br}]^+$ (Eq. 1) at the anode in a mixture of Br^- and Cl^-, since the oxidation potential of Br^- is much less positive than that of Cl^-,[1] if the oxidation to Br· is negligible.[16] Therefore, after a charge Q is passed through a solution of $\mathrm{Br^-+Cl^-}$(r>1), the solution contains halogen species formally with a ratio of $[\mathrm{Br}]^+:\mathrm{Br}^-:\mathrm{Cl}^-=Q/2:1-Q/2:r$. If the formation ratio (R) of the bromochlorinated product to the dibrominated one (thus, the product-selectivity) is proportional to the $\mathrm{Cl^-/Br^-}$ ratio (ratio of Cl^- to Br^- present after electrolysis, i.e. not r but $r/(1-Q/2)$ in the solution undergoing the reaction of Eq. 6), the following equation is obtained:

$$R=\{Q/2\times r/[(1-Q/2)+r]\}/\{Q/2\times(1-Q/2)/[(1-Q/2)+r]\}=r/(1-Q/2). \qquad (7)$$

Equation 7 indicates that R can be given by a simple function of Q and r.

The reaction of **12** gave mixtures of 2-bromo-1-chloro-1-phenylethane (**13**) and 1,2-dibromo-1-phenylethane (**14**) (Eq. 8) in high halogenation efficiencies.



12 **13** **14**

(8)

It could not be confirmed whether the GC peaks for **13** included the 1-bromo-2-chloro isomer. Figure 8 shows both the theoretically calculated and experimental relationships between R(**13**/**14**) and Q at different r's. The calculated and experimental R's agree well with each other when Q and r are not large. Considerable amounts of **14** were formed at Q=2 $\mathrm{F\,mol(Br^-)^{-1}}$ though it theoretically should not be formed, since no unreacted Br^- remained. It is likely that the oxidation of Br^- is not completely exhaustive at Q=2 $\mathrm{F\,mol(Br^-)^{-1}}$ and, consequently, that some Br^- remains unreacted, while some Cl^- is oxidized. However, this could not be the main reason for the formation of **14**, since no dichlorinated product was detected. In addition, even if $[\mathrm{Cl}]^+$ was generated, it should oxidize unreacted Br^- (Eq. 9), because of the much lower electron negativity of bro-

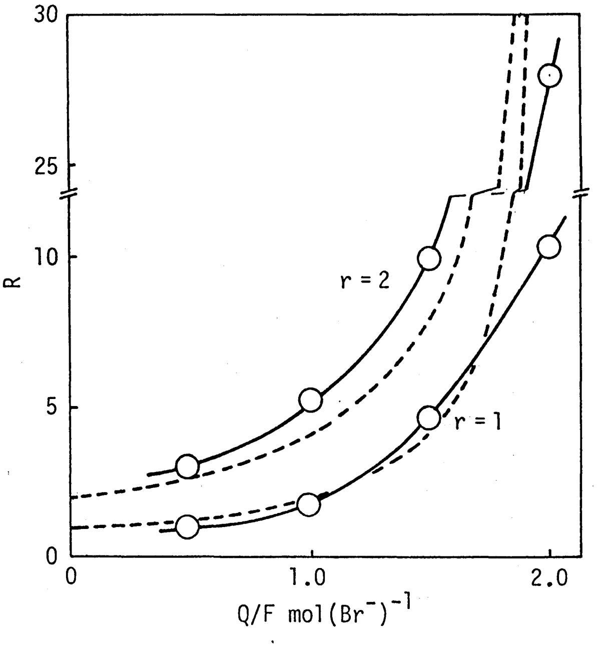


Fig. 8. Relationship between R (formation ratio of **13**/**14**) and Q (amount of charge passed) in the halogenation of **12** (0.1 M) with the BC-reagent generated at r(Cl^-/Br^-)=1 and 2. The concentration of Et_4NBr=0.1 M. The solid lines with circles indicate the experimentally found values; the dotted lines without circles indicate the theoretically calculated values.

mine than chlorine.

$$[Cl]^+ + Br^- \rightarrow Cl^- + [Br]^+ \qquad (9)$$

A further possible reason is that the BC-reagents have Br^--components or cause some radical halogenation.

Although the reaction of **15** also gave mixtures of 1-bromo-2-chloro-cyclohexane (**16**) and 1,2-dibromocyclohexane (**17**) in high halogenation efficiencies, the stereochemistry of the products was not determined. The relationships between R(**16**/**17**) and Q were similar to those given in Fig. 8.

BC-reagents seem to be useful for organic synthesis as oxidizing and halogenating reagents. Furthermore, various kinds of mixed positive halogen reagents may be generated by this anodic method using a variation of combinations of the halide ions (F^-, Br^-, Cl^-, and I^-).

For a comparison with ex-cell electrohalogenation using the BC-reagents, the in-cell electrohalogenation of the olefins was also examined under similar conditions so as to give lower yields; the R's were not simply controlled by Q and r. For instance, the in-cell halogenation of **12** gave considerable amounts of unknown products in addition to **13** and **14**, particularly at large Q and r. The formation of the unknown products is probably due to direct anodic oxidation of the starting **12** and/or the products.

Conclusions

By investigating the halogenation of some test compounds with Br–Cl composite species (BC-reagent) anodically-generated from mixtures of $Br^- + Cl^-$ in CH_2Cl_2 (even though the chemical composition was not specified) we obtained the following important results concerning the reactivity:

(1) The BC-reagent brominates methoxybenzenes; their brominating power can be variably and precisely controlled by the amount of charge (Q) passed and the ratio (r) of Cl^-/Br^- used.

(2) Although aniline is also brominated with the reagent in high bromination efficiency, the brominating power varies over a narrow range.

(3) Olefins give the corresponding dibrominated and bromochlorinated products in high halogenation efficiencies, and their selectivities are variably and precisely controlled by Q and r. The experimental selectivities agree with those theoretically predicted when Q and/or r are not large,

$$R = r/(1 - Q/2),$$

where R is the formation ratio of bromochlorinated/dibrominated products.

Experimental

General. Electrolysis was carried out in a divided glass cell[1] equipped with Pt electrodes (anode, 3×2 cm; cathode, 2×1.5 cm) using a Hokuto HA-501 potentio-galvanostat. ^{1}H NMR, IR, and MS spectra were recorded on a JEOL JNM-PMX60 spectrometer (60 MHz), a Hitachi 285 spectrometer and a JEOL JMS-D100 gas chromatograph-mass (GCMS) spectrometer, respectively. GC analysis was performed using a Yanaco G-2000 gas chromatograph with a Silicone DC-550 column (4 m) at 50—210 °C. Preparative TLC analysis was also performed using silica gel-coated plates/hexane.

Chemicals and Solvent. The starting compounds (**1**, **4**, **8**, **12**, and **15**), supporting electrolytes (Bu_4NClO_4, Et_4NBr, and Et_4NCl), trihalide salts (Bu_4NBr_3, Bu_4NBr_2Cl, and Bu_4NBrCl_2), and standard samples of some (**2**, **3** and **9**—**11**) of the products were commercially supplied. Samples of **5**[20] and **6**[21] were prepared by bromination of **4** with Bu_4NBr_3 and Br_2, respectively. Samples of **13**[12–14] and **14**[22] were prepared by halogenation of **12** with pyridinium hydrobromide-perbromate and Bu_4NBrCl_2, respectively, while those of **16** and **17** were synthesized by halogenation of **15** with Bu_4BrCl_2 and Bu_4NBr_3, respectively. The structures of these compounds were confirmed by their MS spectra, IR spectra, ^{1}H NMR spectra and/or elemental analysis.

CH_2Cl_2, as the electrolytic solvent, was refluxed over CaH_2 and then distilled in an atmosphere of dry nitrogen.

Electrogeneration of BC-Reagents. CH_2Cl_2 solutions (40 cm^3) containing 0.05—0.013 M Et_4NBr+0.5—0.25 M Et_4NCl+0.1 M Bu_4NClO_4 (r=1—5), 0.1 M Et_4NBr+0.1 M Et_4NCl (r=1), and 0.1 M Et_4NBr+0.1—0.2 M Et_4NCl (r=1—2) were used as anolytes for the BC-reagents for halogenation of **1** and **4**, **8**, and **12** and **15**, respectively. The catholyte was 22 cm^3 of 0.1 M Bu_4NClO_4/CH_2Cl_2. Electrolysis was galvanostatically carried out at 5.0 and 8.3 mA cm^{-2} of anodic current densities for **1** and **4**, and **8**, **12** and **15**, respectively, at room temperature in a dry nitrogen atmosphere.

Halogenation. After passage of an appropriate amount of charge [Q<2 F mol(Br$^-$)$^{-1}$], 1.0 equiv mol of **1**, 0.5—1.0 equiv mol of **4** and **8**, or 1.5—6.0 equiv mol of **12** and **15** was added to the anolyte. The resulting reaction mixture was allowed to stand for 24h in the halogenation of **1**, **4**, **12** and **15** and 1 h for **8**, at room temperature in a dry nitrogen atmosphere. Unreacted BC-reagent was decomposed by shaking with a $Na_2S_2O_3$ solution; and then the CH_2Cl_2 phase was dried over $MgSO_4$ and subjected to analysis of the products and unreacted starting compounds.

In a similar manner as that mentioned above, **1** and **4** were also brominated with 1.0 equiv mol of commercially-available Bu_4NBr_3, Bu_4NBr_2Cl or Bu_4NBrCl_2.

Analysis. The products were identified with authentic samples by GCMS, ^{1}H NMR and/or IR, and were quantitatively analyzed by GC.

The authors wish to thank Dr. Toshio Fuchigami of Tokyo Institute of Technology for helpful discussions.

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