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LETTERS

Nuclear Field Shift Effect in the Isotope Exchange Reaction of Chromium(III) Using a Crown Ether

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Chromium isotopes were fractionated by the liquid−liquid extraction system using dicyclohexano-18-crown-6. We found a mass-independent isotope effect that the intermediate isotope of ^{52}Cr was enriched in the organic phase. Because of its magic number neutrons $N = 28$, ^{52}Cr has the smallest nuclear charge distribution in naturally occurring chromium isotopes. The enrichment property gives the confident experimental fact of the nuclear field shift effect in the new Bigeleisen theory.

Introduction

In the research field of isotope chemistry, the conventional mass-dependent theory of the Bigeleisen-Mayer equation[1] has been extended to include the nuclear field shift effect,[2,3]

$$\ln \alpha = \frac{hc}{kT}\nu_{\mathrm{fs}}a + \frac{1}{24}\left(\frac{h}{2\pi kT}\right)^2\frac{\delta m}{mm'}b \tag{1}$$

where ν_{fs} is the field shift, a is the field shift scaling factor, and b is the scaling factor for the vibrational mass effect. The field shift is one kind of isotope shift[4] in orbital electrons, which results from the isotopic difference in nuclear size and shape. The field shift gives an isotope effect via a displacement of electronic molecular state. After the proposal of the new theory, researchers used it in order to explain unusual isotope effects.[5−9] In recent studies on mass-independent isotope effects, some extended interpretations based on the new theory have been discussed.[10−16]

The mass-independent isotope effects reported are mostly on the odd atomic mass isotopes having nuclear spins with finite values.[2,3,5,7−9,17,18] It is difficult to determine these mass-independent isotope effects as the true field shift effect, because an interference due to the Fermi contact interaction must be considered in these cases. The field shift effect should be studied on even atomic mass isotopes whose nuclear spins are zero. In this context, Fujii and co-workers have studied the mass-independent isotope effect in even atomic mass number isotopes.[6,10,11,14] In some elements, however, isotopic change in nuclear charge distribution $\delta\langle r^2\rangle$ shows a linear relationship with mass number, and hence careful treatments have been required to separate the field shift effect and the mass-dependent isotope effect.

Because of its magic number neutrons $N = 28$, an even atomic mass isotope ^{52}Cr has the smallest nuclear charge radius[4,19,20]

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of the stable chromium isotopes, ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr. If a clear field shift occurs, the medium isotope ^{52}Cr should be foremost fractionated according to the Bigeleisen theory. A mass-independent isotope effect of chromium(III) has been found in our previous study.[21] To see a specific enrichment of ^{52}Cr more accurately, we renewed the experimental condition and the isotopic analytical method.

The first publication on the chemical isotope separation with macrocyclic polyether was calcium isotope separation with dicyclohexano-18-crown-6 (DC18C6).[22] In many cases,[23] DC18C6 systems are effective for separating isotopes. For chromium extraction, DC18C6 in 1,2-dichloroethane is one of the typical organic phases for separating Cr(III) and Cr(VI).[24,25] In systems employing concentrated aqueous solutions and macrocyclic polyethers, large mass-independent isotope effects are known to be more commonly observed.[14] Thus, we studied the chromium isotope effect in a liquid−liquid extraction with a concentrated chromium trichloride solution and an organic solution of DC18C6 in 1,2-dichloroethane. In mass spectrometry with a thermal ionization ion source, an accurate isotopic analytical method of the total evaporation method was introduced. In this paper, we present definite evidence of the field shift effect in chromium.

Experimental Section

Dicyclohexano-18-crown-6 was a product of Acros Chimica N.V. (98% purity). 1,2-Dichloroethane (over 99.9% purity) was purchased from Merck KGaA. Chromium trichloride (hydrous, 99.99% purity) was purchased from Kojundo Chemical Laboratory Co., Ltd. To avoid the isotopic interference of other first-low transition metals in mass spectrometry, especially ^{54}Fe interference on ^{54}Cr, pure water and nitric acid were purchased from Kanto Chemical Co., Inc. The concentration of each metallic impurity in these reagents was certified to be under 0.01 ppb. Chromium trichloride was dissolved in pure water to create a solution, 4 mol dm^{-3} (M) $CrCl_3$. The organic phase was 0.1 M DC18C6 in 1,2-dichloroethane. Before the experiments, the organic phase was scrubbed twice with the pure water to remove any kinds of hydrophilic organic impurities.

A 1 cm^3 (mL) aqueous solution and 10 mL organic solution were mixed in a glass vial with a stirrer bar, and the glass vial was sealed with a stopcock. The two phases were stirred by a magnetic stirrer for 30 min. After the fore-extraction, the two phases were separated by centrifugation (1500 rpm, 1 min). An 8 mL aliquot of the upper organic solution was taken for back-extraction. The extracted chromium in the separated organic phase was stripped into 8 mL of pure water. The back-extraction was performed in the same manner of the fore-extraction. After the two phases were separated by centrifugation, 6 mL of the upper aqueous phase was taken. This solution was scrubbed twice with 6 mL of pure 1,2-dichloroethane to prepare an organic free sample for mass spectrometry. These procedures were carried out at 301 ± 1 K. The chromium concentration in the back-extraction water was analyzed by ICP-AES (Shimadzu, ICPS-1000TR). The same liquid−liquid extraction experiment was performed three times. The distribution ratio was determined to be $(8.8 \pm 0.2) \times 10^{-6}$. For the kinetics of the extraction of Cr(III), in an efficient solvent extraction system,[26,27] 15 min has been reported as the optimum time to secure the extraction equilibrium. In our case, no change in the D value was observed in periods over 30 min.

For the measurement of chromium isotope ratios by a thermal ionization mass spectrometer, isotope fractionation in the evaporation process is a significant problem.[28] The total evaporation method was applied to the present study, which is accepted in uranium isotopic analysis[29] as a fractionation bias free measurement. The back-extraction solution was heated to dryness, and a chromium solution containing 50 ppm Cr in 1 M HNO_3 was prepared. Each 10 μL aliquot was put on a sample filament, in which the filament used was rhenium ribbon prepared via zone melting. The total amount of Cr loaded on the filament was 500 ng. The filament with 500 ng of Cr of the standard reference material NIST-SRM979 was also prepared in the same manner. The isotopic analysis was performed using a mass spectrometer with a multicollector system (Finnigan, MAT262).

TABLE 1: Measurement Results of NIST-SRM979

	^{50}Cr/^{52}Cr	^{53}Cr/^{52}Cr	^{54}Cr/^{52}Cr
total evaporation	0.051647	0.11368	0.028321
	±0.000105	±0.00011	±0.000058
certified value[30]	0.05186	0.11339	0.02822
	±0.00010	±0.00015	±0.00006
% rel difference to ref	−0.41	+0.26	+0.36

A rhenium double filament was loaded into the mass spectrometer. Because the natural abundance of ^{52}Cr (83.79%) is greatest, its ion beam was monitored and ^{m}Cr/^{52}Cr was measured (the superscript m means mass number 50, 52, 53, or 54). The ion beam intensity at mass number 51 was also checked to monitor the background. The measurement protocol for total evaporation used in this study was as follows. The ionization filament was heated to 4 A in 10 min. The sample (evaporation) filament was heated to attain a 2×10^{-13} A ion current of ^{52}Cr, and then peak centering and focusing were quickly done. The measurement was performed with the increase of the sample filament current by 10 mA/scan, in which the integration time of 1 scan was 4 s. The upper limit of the ^{52}Cr ion current was set at 7.5×10^{-11} A. The data acquisition was terminated when the ^{52}Cr ion current fell below 2×10^{-13} A.

Since the total ion current was integrated in the total evaporation measurement, one measurement gives no error of isotopic fractionation. Hence, we evaluated the reproducibility as an experimental error. Seven samples of NIST-SRM979 and 8 samples of the stock solution were analyzed. The averaged value of each isotope ratio was determined, and the standard error (SE) of 2SE was calculated. We performed the same extraction experiment three times, and each back-extracted sample was analyzed three to five times. In total, 10 samples were analyzed. The 2SE of the measured isotopic ratio was 0.26% or better.

Results and Discussion

Measurement results of NIST-SRM979 by total evaporation method are shown in Table 1. The certified values[30] of NIST-SRM979 by conventional method are shown together with the standard deviations (SD) of 2SD. Our results show good agreement with the certified values within the experimental errors of 2−3SD. Since the total evaporation method is the fractionation bias free measurement, the difference shown in Table 1 would be due to a specific machine bias in our system. The difference in each isotope ratio is determined to be ±0.41% or smaller. This is acceptable considering the uncertainties in the conventional measurement with a thermal ionization mass spectrometer.[31,32] The errors determined in the present study show values similar to those of the certified values. In the present system, about 7 samples must be analyzed in order to bring the SE value close to the SD value of the certified value.

Table 2 shows the measurement results of the stock solution and the back-extraction solution. Beyond 2SE, obvious changes

TABLE 2: Measurement Results of Stock Solution and Back-Extraction Solution

	$^{50}Cr/^{52}Cr$	$^{53}Cr/^{52}Cr$	$^{54}Cr/^{52}Cr$
stock solution	0.052310	0.11351	0.028266
	±0.000093	±0.00005	±0.000028
back-extraction solution	0.052075	0.11330	0.028165
	±0.000117	±0.00013	±0.000074

TABLE 3: Isotope Separation Factors and Isotope Enrichment Factors

	^{50}Cr	^{52}Cr	^{53}Cr	^{54}Cr
$\alpha_{52,m}$	0.9955	1	0.9981	0.9964
	±0.0028		±0.0015	±0.0028
$\epsilon_{52,m}$	−0.0045	0	−0.0019	−0.0036
	±0.0028		±0.0015	±0.0028

in the isotope ratios can be seen. If a contamination of Ti(^{50}Ti), V(^{50}V), and/or Fe(^{54}Fe) occurs, $^{50}Cr/^{52}Cr$ and/or $^{54}Cr/^{52}Cr$ in the back-extraction solution must be overestimated. Both $^{50}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ in the back-extraction solution were smaller than those in the stock solution. Hence, it can be concluded that, throughout the study, there is no isotopic interference due to a contamination of metallic impurities. The differences in isotope ratios shown in Table 2 are due to the chemical isotope effect via the ligand exchange reaction.

The isotope separation factor α is defined:

$$\alpha_{52,m} = \frac{([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{org}}}{([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{aq}}} \qquad (2)$$

where $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{org}}$ and $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{aq}}$ are the isotope ratios of ^{m}Cr relative to ^{52}Cr found in the organic and aqueous phases, respectively. In the present study, since the distribution ratio is so low, $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])$ in the stock solution can be substituted for $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{aq}}$. The isotope enrichment factor ϵ is defined

$$\epsilon_{52,m} = \alpha_{52,m} - 1 \qquad (3)$$

Considering the magnitude of the isotope effect, an approximation, $\alpha - 1 \approx \ln \alpha$, can be used. The detailed theoretical background of the isotope separation factor can be seen elsewhere.[1,33] Since the machine biases are canceled out, the α value can be calculated from the raw data shown in Table 2 using eq 2. Calculated α values and ϵ values are shown in Table 3. All $\epsilon_{52,50}$, $\epsilon_{52,53}$, and $\epsilon_{52,54}$ are negative, implying that ^{52}Cr is enriched in the organic phase.

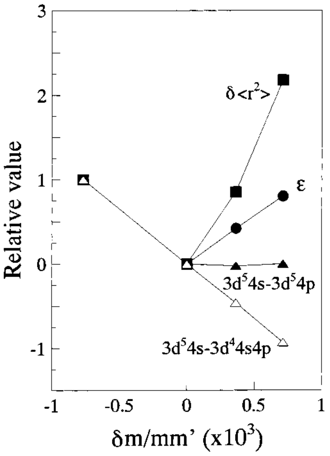

Figure 1. Relative changes in isotope enrichment factor and nuclear charge radius, and relative isotope shifts in Cr I. The changes in mean-square radius are reproduced from the data reported by Wohlfahrt et al.[19,20] The relative isotope shifts in Cr I are calculated from the data reported by Bruck et al.[34,35] Values for the isotope pair ^{50}Cr−^{52}Cr were normalized to be unity.

Changes in the mean-square radius of chromium, $\delta\langle r^2\rangle$, reported by Wohlfahrt et al.[19,20] are shown in Figure 1 as functions of $\delta m/mm'$. The experimental results of $\epsilon_{52,m}$ are shown together. Isotope shifts of Cr I in a $3d^54s-3d^54p$ transition and a $3d^54s-3d^44s4p$ transition measured by Bruck et al.[34,35] are also shown. To facilitate comparison, all data for the isotope pair ^{50}Cr−^{52}Cr were normalized to be unity. The isotope shifts in the $3d^54s-3d^44s4p$ transition show a strong dependence on the mass difference. The isotope shift is composed of two major shifts, i.e., the mass shift and the field shift.[4] The mass shift, which is proportional to $\delta m/mm'$, is predominant in the $3d^54s-3d^44s4p$ transition. Because of its large density distribution in the nucleus, the s-orbital electron is strongly affected by the field shift, which is proportional to $\delta\langle r^2\rangle$. Hence, in the $3d^54s-3d^54p$ transition, the breakdown of the linear dependency of $\delta m/mm'$ is due to the field shift. In every chemical exchange reaction, if a transition of electronic molecular states is strongly affected by the field shift, the obtained isotope effect should show a mass-independent isotope effect having the characteristic of $\langle r^2\rangle$. From Figure 1, it can be concluded that a clear field shift effect was found in the chromium isotope effect by using concentrated $CrCl_3$ solution and DC18C6 in 1,2-dichloroethane.

This study presents a prospect for future progress of mass-independent isotope effect. Under similar conditions, multistage extraction or liquid chromatography more effectively demonstrates larger isotope effect. Much more precise isotopic analysis with high accuracy is essential for this research field.

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References and Notes

(1) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261−267.

(2) Bigeleisen, J. *J. Am. Chem. Soc.* **1996**, *118*, 3676−3680.

(3) Nomura, M.; Higuchi, N.; Fujii, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9127−9130.

(4) King, W. H. *Isotope Shifts in Atomic Spectra*; Plenum Press: New York, 1984.

(5) Nishizawa K.; Miki, T.; Ikeda, R.; Fujii, T.; Yamamoto, T.; Nomura, M. *J. Mass Spectrom. Soc. Jpn.* **1997**, *45*, 521−527.

(6) Fujii, T.; Yamamoto, T.; Nishizawa, K.; Inagawa, J.; Gunji, K.; Watanabe, K. *Solvent Extr. Ion Exch.* **1998**, *16*, 985−999.

(7) Dembinski, W.; Poninski, M.; Fiedler, R. *Sep. Sci. Technol.* **1998**, *33*, 1693−1701.

(8) Mioduski, T. *Comments Inorg. Chem.* **1999**, *21*, 175−196.

(9) Ismail, I. M.; Fukami, A.; Nomura, M.; Fujii, Y. *Anal. Chem.* **2000**, *72*, 2841−2845.

(10) Fujii, T.; Yamamoto, T.; Inagawa. J.; Gunji, K.; Watanabe, K.; Nishizawa, K. *Solvent Extr. Ion Exch.* **1999**, *17*, 1219−1229.

(11) Fujii, T.; Yamamoto. T.; Inagawa, J.; Gunji, K.; Watanabe, K.; Nishizawa, K. *Solvent Extr. Ion Exch.* **2000**, *18*, 1155−1166.

(12) Fujii, T.; Yamamoto, T.; Inagawa, J.; Watanabe, K.; Nishizawa. K. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 663−669.

(13) Fujii, T.; Inagawa, J.; Nishizawa, K. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1880−1885.

(14) Fujii, T.; Hirata. T.; Shibahara, Y.; Nishizawa, K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3125−3129.

(15) Bigeleisen, *J. Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 4808−4809.

(16) Knyazev, D. A.; Semin, G. K., Bochkarev, A. V. *Polyhedron* **1999**, 18, 2579−2582.

(17) Nishizawa, K.; Nakamura, K.; Yamamoto, T.; Masuda, T. *Solvent Extr. Ion Exch.* **1993**, *11*, 389−394.

(18) Nishizawa, K.; Nakamura, K.; Yamamoto, T.; Masuda, T. *Solvent Extr. Ion Exch.* **1994**, *12*, 1073−1084.

(19) Wohlfahrt, H. D.; Shera, E. B.; Hoehn, M. V.; Yamazaki, T.; Steffen, R. M. *Phys. Rev. C* **1981**, *23*, 533−548.

(20) Aufmuth, P.; Heilig, K.; Steudel, A. *Atom. Data Nucl. Data Tables* **1987**, *37*, 455−490.

(21) Kawashiro, F.; Fujii, T.; Nishizawa, K. *Proceedings of 6th Workshop on Separation Phenomena in Liquids and Gases*, Nagoya, Japan, Oct 18−21, 1998; Yamamoto, I., Ed.; Nagoya University: Nagoya, Japan, 1998; pp 391−399.

(22) Jepson, B. E.; DeWitt, R. *J. Inorg. Nucl. Chem*. **1976**, *38*, 1175−1177.

(23) Tsivadze, A. Yu.; Zhilov, V. I.; Demin, S. V. *Russ. J. Coord. Chem*. **1996**, *22*, 229−237.

(24) Koshima, H.; Onishi, H. *Anal. Sci*. **1993**, *9*, 141−142.

(25) Yakshin, V. V.; Vilkova, O. M.; Makarova, L. T. *J. Anal. Chem*. **1998**, *53*, 409−411.

(26) Majumdar, S. K.; De, A. K. *Anal. Chem*. **1960**, *32*, 1337−1339.

(27) De, A. K.; Khopkar, S. M.; Chalmers, R. A. *Solvent Extraction of Metals*; VNR: London, 1970.

(28) Ball, J. W.; Bassett, R. L. *Chem. Geol*. **2000**, *168*, 123−134.

(29) Fiedler, R.; Donohue, D.; Grabmueller, G.; Kurosawa, A. *Int. J. Mass Spectrom. Ion Processes* **1994**, *132*, 207−215.

(30) Shields, W. R.; Murphy, T. J.; Catanzaro, E. J.; Garner, E. L. *J. Res. Natl. Bur. Stand.* **1966**, *70A*, 193−197.

(31) De Bièvre, P.; Gallet, M.; Holden, N. E.; Lynus Barnes, I. *J. Phys. Chem. Ref. Data* **1984**, *13*, 809−891.

(32) Platzner, I. T. *Modern Isotope Ratio Mass Spectrometry*; John Wiley & Sons: Chichester, U.K., 1997.

(33) Criss, R. E. *Principles of Stable Isotope Distribution*; Oxford University Press: New York, 1999.

(34) Bruch, R.; Heilig. K.; Kaletta, D.; Steudel, A.; Wendlandt, D. *J. Phys. (Paris)* **1969**, *30*, C1−51−58.

(35) Heilig, K.; Steudel. A. *Atom. Data Nucl. Data Tables* **1974**, *14*, 613−638.