Chemical Characterization of a Volatile Dubnium Compound, DbOCl₃

Nadine M. Chiera,* Tetsuya K. Sato,* Robert Eichler, Tomohiro Tomitsuka, Masato Asai, Sadia Adachi, Rugard Dressler, Kentaro Hirose, Hiroki Inoue, Yuta Ito, Ayuna Kashihara, Hiroyuki Makii, Katsuhisa Nishio, Minoru Sakama, Kaori Shirai, Hayato Suzuki, Katsuyuki Tokoi, Kazuaki Tsukada, Eisuke Watanabe, and Yuichiro Nagame

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1. Experimental details

For the synthesis and the chemical characterization of DbOCl₂, two experimental campaigns were conducted at the JAEA Tandem Accelerator, between 2018 and 2019. In both series of experiments, a 248CmO₂ target (0.55 mg cm⁻²) deposited on a Be backing foil (1.955 mg cm⁻²) was irradiated with a 19F⁺ ion beam (121 MeV primary energy). The beam energy at the middle of the target thickness was calculated with SRIM-2008 [1] to be 103 MeV. During the entire experimental campaign, an overall beam dose of 3.16 × 10¹⁷ 19F⁺ particles was accumulated. A more detailed schematic of the IGC setup coupled to the MANON system [2] is given in Figure S1. The radionuclides produced in the nuclear fusion reactions were thermalized and transported from the target chamber to the quartz column by a He/N₂ (0.9/0.1 volume ratio, 1000 mL min⁻¹) carrier gas. SOCl₂ vapors transported by a N₂/O₂ (0.99/0.01 volume ratio, 200 mL min⁻¹) gas stream were added to the carrier gas as oxychlorinating agents before the reaction furnace Section I of the quartz column, kept at 1000 °C. The pathway of the oxychlorinating agent is highlighted in red in Figure S1. Any non-volatile species was retained on the quartz wool plug placed in the middle of Section I. The volatile oxychloride species were transported to Section II of the quartz column (length: 520 mm, internal diameter: 4 mm) by the carrier gas, where the isothermal chromatography was conducted. The temperature of the chromatographic column, T_iso, was varied in the range of 350 °C to 600 °C. The oxychlorides exiting the gas-chromatographic column were then mixed in the clustering chamber with an inert gas stream loaded with aerosol particles (KCl in He, 2800 mL min⁻¹). The clustering chamber was externally water-cooled to reduce losses of the investigated species by diffusion to its walls. From the clustering chamber, the aerosol particles carrying the oxychloride species were subsequently transported through a 25 m long capillary tube to the collection site of the MANON system within about 2 s. The aerosols were deposited on polyethylene terephthalate (PET) foils (thickness: 120 µg cm⁻²; 20 mm diameter) at the periphery of an 80-position wheel of 80 cm diameter. The wheel was enclosed in an evacuated stainless-steel chamber (internal pressure <10 mbar). The wheel was periodically rotated to position the foils between 6 pairs of Si-PIN α-particles detectors. Each detector had an active area of 18 × 10 mm², and a geometrical detection efficiency of 40% for α-particles. Further information on the IGC setup can be found in [3, 4]. In order to monitor the efficiency of the IGC apparatus, 50 µg cm⁻² of 152Gd were added to the target to simultaneously produce the γ-emitter 168Ta (T₁/₂ = 2.0 min, Eγ = 124.10 keV, Iγ = 33%) in the nuclear fusion reaction 152Gd(19F, 3n)168Ta. Prior and after each experimental run, the 168TaOCl₃ exiting the chromatographic column was collected and its amount was quantified by γ-spectrometry. Therefore, a three-way valve was installed along the capillary tube, allowing for switching between MANON and an aerosol collector equipped with glass-fiber filter disks. In the external chromatogram obtained for 168TaOCl₃, depicted in Figure S2, no variations of the beam energy, target integrity, window foil thickness, and/or gas composition were observed. Therefore, a constant production rate and transport efficiency of 262Db in the 19F⁺ induced nuclear reaction during the entire experiment is expected. As observed in model experiments with NbOCl₃ and TaOCl₃ [4], and as depicted in Figures 2 and S2, the clustering efficiency decreases when the isothermal temperature exceeds 550 °C. In fact, the temperature of the gas in the cluster chamber influences the partition of the oxychloride molecules between the gas phase, the aerosol surface, and the walls of the cluster chamber itself. It follows that the decrease in the overall yield in the external chromatogram at 600 °C is not a consequence of the interaction between the molecules and the chromatographic surface. The same effect was observed for DbOCl₂, and hence, the runs conducted at 600 °C were excluded from the statistical analysis described in Paragraph “3. Statistical analysis of the observed 262Db-258Lr events.”
Figure S1. Schematic of the IGC setup coupled to the MANON system for the chemical exploration of DbOCl₃. See text for details.

Figure S2. Relative yield of TaOCl₃ (open circles) as a function of the isothermal temperature in the chromatographic column. The Monte-Carlo simulation (solid line) was performed using the $\Delta H_{ads} = 128$ kJ mol$^{-1}$ value obtained in [4]. The grey area represents the 68% confidence band ($\pm 5$ kJ mol$^{-1}$) of the $\Delta H_{ads}$ value. Note the drop at the highest temperature due to the inefficient clustering process at high temperatures.

2. Observed $^{262}$Db-$^{258}$Lr events
Throughout the entire experimental campaign, 24 events (i.e., timely correlated detections of consecutive α particles, corresponding to the $^{262}\text{Db} \rightarrow ^{258}\text{Lr} \rightarrow ^{254}\text{Md}$ decay chain) were recorded. The spontaneous fission (SF) decay mode could not be registered by the used measurement electronic system. Details are listed in Table S1. The estimation of the α-energy resolution was performed by analyzing a $^{244}\text{Cm}$ (α-branching ratio: 99%; $E_\alpha (I_\alpha = 77\%) = 5805$ keV) α-spectrum source. In a conservative approximation, 95% of the $^{244}\text{Cm}$ α-decays falls within the energy range $5350 < E_\alpha < 5965$ keV (Figure S3). Thus, the variation of energy from $E_\alpha$ is estimated being $\Delta E_+ = +160$ keV and $\Delta E_- = -455$ keV. The observed tailing of the spectral shape derives from the energy lost by the α-particle while traversing both the deposited KCl aerosol spot and the PET foil, whereas the energy gain can be attributed to pile-up signals of quasi-coincident α and β-decays and electronic noise. By implementing the so-found $\Delta E$ to the known decay properties of $^{262}\text{Db}$ (see Figure S4), the following energy windows for searching $^{262}\text{Db}$ and $^{258}\text{Lr}$ α-decays were adopted:

- $^{262}\text{Db}$:
  - $8005$ keV < $E_{\alpha 1}$ < $8620$ keV ($I_\alpha = 70\%$)
  - $8225$ keV < $E_{\alpha 1}$ < $8840$ keV ($I_\alpha = 30\%$)

- $^{258}\text{Lr}$:
  - $8110$ keV < $E_{\alpha 2}$ < $8725$ keV ($I_\alpha = 20\%$)
  - $8140$ keV < $E_{\alpha 2}$ < $8755$ keV ($I_\alpha = 46\%$)
  - $8166$ keV < $E_{\alpha 2}$ < $8781$ keV ($I_\alpha = 25\%$)
  - $8199$ keV < $E_{\alpha 2}$ < $8814$ keV ($I_\alpha = 9\%$)

The correlation time ($t_{\text{corr}}$) is defined as the time elapsed between two detected α-particles assigned to the decay of $^{262}\text{Db}$ and $^{258}\text{Lr}$, in this very same order. The upper limit for $t_{\text{corr}}$ was established as 5 times the half-life of $^{258}\text{Lr}$, thus covering 97.5% of the decays.

Table S1. List of events assigned to the decay chain $^{262}\text{Db} \rightarrow ^{258}\text{Lr} \rightarrow ^{254}\text{Md}$ detected throughout the entire experimental campaign. The energy of the mother nuclide $^{262}\text{Db}$ ($E_{\alpha 1}$), the energy of the daughter nuclide $^{258}\text{Lr}$ ($E_{\alpha 2}$), the correlation time ($t_{\text{corr}}$), and the temperature of the chromatographic column ($T_\text{iso}$) at which each event was observed are specified.

| Event | $E_{\alpha 1}$ (keV) | $E_{\alpha 2}$ (keV) | $t_{\text{corr}}$ (s) | $T_\text{iso}$ (°C) |
|-------|----------------------|----------------------|----------------------|----------------------|
| 1     | 8322                 | 8461                 | 8.05                 | 600                  |
| 2     | 8331                 | 8331                 | 3.09                 | 600                  |
| 3     | 8222                 | 8394                 | 10.78                | 600                  |
| 4     | 8638                 | 8552                 | 5.29                 | 600                  |
| 5     | 8103                 | 8130                 | 7.03                 | 600                  |
| 6     | 8352                 | 8373                 | 3.68                 | 550                  |
| 7     | 8361                 | 8419                 | 0.04                 | 550                  |
| 8     | 8787                 | 8781                 | 6.43                 | 550                  |
| 9     | 8425                 | 8605                 | 2.72                 | 550                  |
| 10    | 8544                 | 8785                 | 7.67                 | 550                  |
| 11    | 8731                 | 8787                 | 4.18                 | 550                  |
| 12    | 8636                 | 8268                 | 1.62                 | 450                  |
| 13    | 8769                 | 8752                 | 5.20                 | 450                  |
| 14    | 8220                 | 8791                 | 4.22                 | 450                  |
| 15    | 8801                 | 8742                 | 6.81                 | 400                  |
| 16    | 8714                 | 8286                 | 13.13                | 400                  |
| 17    | 8018                 | 8754                 | 0.44                 | 400                  |
| 18    | 8490                 | 8730                 | 3.26                 | 400                  |
Figure S3. \(^{244}\)Cm \(\alpha\)-peak shape at \(E_\alpha = 5805\) keV. The area where 95% of the \(^{244}\)Cm \(\alpha\)-decay was recorded is shaded. The latter is limited by a maximum \(\alpha\)-energy \((E_{\alpha,\text{max}})\) of 5965 keV and a minimum \(\alpha\)-energy \((E_{\alpha,\text{min}})\) of 5350 keV. In a conservative approximation, the detected \(\alpha\)-particles are thus affected by a possible energy loss of 455 keV, and an energy increase of 160 keV.
Figure S4. Decay properties of $^{262}$Db ($t_{1/2} = 34 \text{ s}$) and its daughter nuclide $^{258}$Lr ($t_{1/2} = 3.5 \text{ s}$). SF = spontaneous fission (green); EC = electron capture (red); $\alpha$ = $\alpha$-decay (yellow). $I_\alpha$ = intensity (also refer to as emission probability) of the associated $\alpha$-decay energy. Data taken from [5].

3. Statistical analysis of the observed $^{262}$Db-$^{258}$Lr events

To ensure statistical significance of the observed events, it is necessary to determine the number of expected “background $\alpha$-decays” within the energy region of interest, i.e., the amount of consecutive $\alpha$-particles detected by the instrument (within the searched energy and time window) that do not necessarily correspond to the decay of the nuclides of interest. The presence of a significant background may lead to the observation of random correlations, i.e., inauthentic decay chains resulting from genetically unrelated $\alpha$-decays, which did not originate thus from the consecutive decays of the investigated superheavy nuclides. The occurrence of random correlations can be described by a Poisson distribution if accidentally two background $\alpha$-particles appear within the correlation time window $t_{corr}$. The rate of background $\alpha$-particles ($\beta$) detected during $t_{meas}$ can be estimated as:

$$\beta = \frac{(N_{\alpha} - 2N_{\alpha-corr})}{S \cdot t_{meas}} \cdot \frac{1}{2} \cdot \left( \frac{S \cdot t_{corr}}{2} \right) \cdot e^{-\beta \cdot t_{corr}}$$

with $N_{\alpha}$ - total number of $\alpha$-decays in the $\alpha$-decay energy range of $^{262}$Db and $^{258}$Lr;
$N_{\alpha-corr}$ - number of correlated $\alpha$-decays in the $\alpha$-decay energy range of $^{262}$Db and $^{258}$Lr;
$S$ - total number of aerosol spots deposited in MANON.

The total number of registered $\alpha$-particles contains the number of $\alpha$-particles observed as part of the correlated decay chains. The number of random correlations $N_{rand}$ can be calculated as follows:

$$N_{rand}(S, \beta, t_{meas}, t_{corr}) = 2 \cdot S \cdot t_{meas} \cdot \left( \frac{S \cdot t_{corr}}{2} \right) \cdot e^{-\beta \cdot t_{corr}}$$

The factor 2 in Equation (S2) accounts for the fact that the $\alpha$-particles of $^{262}$Db and $^{258}$Lr are emitted in an overlapping energy range, being thus indistinguishable from each other. As shown in Table S2, the expected number of random correlations $N_{rand}$ at each $T_{iso}$ is lower than 0.4, and therefore, the subsequent statistical analysis was performed assuming that all the observed event chains represent true correlations of consecutive $\alpha$-decays of $^{262}$Db and $^{258}$Lr, and no random correlations were present. For simplicity reasons, all the experimental runs performed at the very same $T_{iso}$ were considered as obtained by a single sample collected for a time $t_{coll}$, and whose
activity was measured by six pairs of α-detectors during a total detection period $t_{\text{meas}}$ (also referred to as “measurement interval”). Such simplification is possible only if the probability of recording random correlations is sufficiently low.

Table S2. Expected number of random correlations ($N_{\text{rnd}}$) at each isothermal temperature ($T_{\text{iso}}$). $N_{\alpha \alpha}$: number of observed α-α correlations assigned to the decay chain $^{262}\text{Db} \rightarrow ^{258}\text{Lr} \rightarrow ^{254}\text{Md}$. $S$: number of aerosol spots deposited on the MANON wheel during all the runs conducted at the very same $T_{\text{iso}}$. $N_{\alpha}$: number of α-decays in the α-decay energy range of Db and Lr.

| $T_{\text{iso}}$ (°C) | $N_{\alpha \alpha}$ | $S$ | $N_{\alpha}$ | $N_{\text{meas}}$ |
|----------------------|---------------------|-----|--------------|------------------|
| 550                  | 6                   | 5887| 96           | 0.224            |
| 450                  | 3                   | 4498| 49           | 0.080            |
| 400                  | 4                   | 5541| 114          | 0.397            |
| 375                  | 6                   | 11057| 83           | 0.089            |
| 350                  | 0                   | 12730| 153          | 0.361            |

For the calculation of the relative chemical yields at each $T_{\text{iso}}$, it is needed to derive an a posteriori conditional probability function that allows to deduce the deposition rate $\kappa$ of $^{262}\text{Db}$ in the aerosol spots in dependence of the observed number $N_{\alpha \alpha}$ of α-α correlations (also referred to as “events”). The deposition rate $\kappa$ represents the average rate of $^{262}\text{Db}$ atoms deposited in the MANON spots at a given isothermal temperature $T_{\text{iso}}$ per accumulated beam dose $\mathcal{D}$, and it includes all experimental losses including the retention losses in the isothermal chromatography column. In a first step, an a priori probability is derived that allows forecasting the number of events $N_{\alpha \alpha}$ under the condition that the deposition rate $\kappa$ is well known. In a second step, a posteriori probability function is deduced using the Bayes theorem. This conditional probability allows for estimating the value of the deposition rate $\kappa$, under the condition that the number of observed events $N_{\alpha \alpha}$ is exactly known.

Assuming a constant deposition rate $\kappa$, the probability $P_{\text{dep}}$ that $N$ atoms of $^{262}\text{Db}$ were deposited on a sample during $t_{\text{coll}}$ can be calculated following a Poisson distribution with the distribution parameter ($\kappa \cdot \mathcal{D}$):

$$P_{\text{dep}}(N | \kappa) = \frac{(\kappa \cdot \mathcal{D})^N}{N!} \cdot e^{-\kappa \cdot \mathcal{D}}$$

(S3)

It needs to be taken into consideration that a fraction of the $^{262}\text{Db}$ atoms deposited during $t_{\text{coll}}$ might have decayed before the measurement starts, and hence, those decays were not detected. The average survival probability $P_{\text{surv}}$ of a $^{262}\text{Db}$ atom deposited during $t_{\text{coll}}$ is:

$$P_{\text{surv}}(t_{\text{coll}}) = \frac{1}{\lambda_{\text{Db} \cdot t_{\text{coll}}}} \cdot \left(1 - e^{-\lambda_{\text{Db} \cdot t_{\text{coll}}}}\right)$$

(S4)

with $\lambda_{\text{Db}}$ – decay constant of $^{262}\text{Db}$

Considering $P_{\text{surv}}$, it is possible to estimate the conditional probability $P_{\text{sample}}(M | N)$ that $M$ atoms of $^{262}\text{Db}$ were present at the beginning of the measurement interval (i.e., that they did not decay during $t_{\text{coll}}$), in dependence of the number $N$ of atoms of $^{262}\text{Db}$ deposited on a sample:

$$P_{\text{sample}}(M | N) = \binom{N}{M} \cdot P_{\text{surv}}(t_{\text{coll}})^M \cdot \left(1 - P_{\text{surv}}(t_{\text{coll}})\right)^{N-M}$$

(S5)

The number of $M$ atoms existing at the beginning of the measurement interval is ultimately dependent on the deposition rate $\kappa$, previously defined. Thus, the conditional probability $P_{\text{sample}}(M | \kappa)$ can be deduced as:

$$P_{\text{sample}}(M | \kappa) = \sum_{N=M}^{\infty} P_{\text{sample}}(M | N) \cdot P_{\text{dep}}(N | \kappa)$$

(S6)

It follows a Poisson distribution with the distribution parameter ($\kappa \cdot \mathcal{D} \cdot P_{\text{surv}}(t_{\text{coll}})$).
The detection probability of an α-α correlation depends on parameters such as the decay constants \( \lambda_{\text{Db}} \), \( \lambda_{\text{Lr}} \), the α-decay intensities \( v_{\text{Db}} \), \( v_{\text{Lr}} \), and the detection probabilities \( \epsilon_{\text{Db}} \), \( \epsilon_{\text{Lr}} \) of the mother isotope \(^{262}\text{Db}\) as well as its daughter \(^{258}\text{Lr}\), respectively. These parameters can be mathematically combined in a single expression (xve):

\[
(xve) = \frac{(1-e^{-2\lambda_{\text{Db}}t_{\text{meas}}})\lambda_{\text{Db}}(1-e^{-2\lambda_{\text{Db}}t_{\text{meas}}})\lambda_{\text{Lr}}}{\lambda_{\text{Db}}-\lambda_{\text{Lr}}} \cdot v_{\text{Db}} \cdot v_{\text{Lr}} \cdot \epsilon_{\text{Db}} \cdot \epsilon_{\text{Lr}}
\]

Finally, the conditional probability \( P_{\text{events}}(N_{\alpha\alpha} | \kappa) \) to register \( N_{\alpha\alpha} \) correlated α-α-decays – given the condition of well-known \( \kappa \) – can be expressed as a Poisson distribution:

\[
P_{\text{events}}(N_{\alpha\alpha} | \kappa) = \frac{(\kappa \cdot P_{\text{surv}}(t_{\text{coll}}))^{N_{\alpha\alpha}}}{N_{\alpha\alpha}!} \cdot e^{-\kappa \cdot P_{\text{surv}}(t_{\text{coll}}) \cdot (xve)}
\]  

(S9)

By defining

\[
D = D \cdot P_{\text{surv}}(t_{\text{coll}}) \cdot (xve)
\]

(S10)

Equation (S9) can be written in absolute analogy to Eq. (S3) as:

\[
P_{\text{events}}(N_{\alpha\alpha} | \kappa) = \frac{(\kappa \cdot D)^{N_{\alpha\alpha}}}{N_{\alpha\alpha}!} \cdot e^{-\kappa \cdot D}
\]  

(S11)

Equation (S11) allows for calculating the expected number of events given a certain deposition rate for each isothermal temperature, but requires the exact knowledge of \( \kappa \). One needs to bear in mind that the experimental deposition rate \( \kappa \) is connected to the production rate of \(^{262}\text{Db}\) by the overall chemical yield \( Y_{\text{chem}} \). The latter contains the probabilities for the nuclear reaction products to be transported from the recoil chamber to the oxychlorination section, to form the oxychloride, to pass and exit the gas-chromatographic column, to be attached to the KCl aerosols, for finally being deposited on the PET foil in MANON. The value of the deposition rate \( \kappa \) can be expressed as:

\[
\kappa = Y_{\text{chem}} \cdot \frac{N}{\delta} \cdot P_{\text{surv}}(t_{\text{coll}}) \cdot (xve)
\]  

(S12)

with \( N \) – production rate of \(^{262}\text{Db}\).

Equation (S12) can be expressed as well as a function of the deposition rate without the isothermal chromatographic column \( (k_{\delta}) \) and the absolute chemical yield of the isothermal chromatography, \( Y_{\text{gc}} \). For a chromatographic column of length \( l \) it is obtained:

\[
\kappa = Y_{\text{gc}} \left( \frac{1}{\Delta H_{\text{ads}}} \right) \cdot k_{\delta} \cdot T_{\text{iso}}
\]  

(S13)

Under the assumption that also at high temperatures (i.e., \( T_{\text{iso}} = 550 \, ^{\circ}\text{C} \)) no loss occurs and thus no significant changes in the chemical yield are observed, i.e., \( \lim_{T_{\text{iso}} \to \infty} Y_{\text{gc}} \left( \frac{1}{\Delta H_{\text{ads}}} \right) = 1 \), \( k_\delta \) is equivalent to the deposition rate in the high temperature limit \( k_\alpha \). Hence, the application of Equation (S12) for the deduction of the relative yields at each \( T_{\text{iso}} \) requires that either 1) \( Y_{\text{chem}} \); or 2) \( k_\delta \) and \( Y_{\text{gc}} \); or 3) \( k_\alpha \) are well known. In order to construct a trustworthy external chromatogram from experimental results, it is mandatory to deduce the relative yields at each \( T_{\text{iso}} \) as a function of the deposition rate \( \kappa \), which is in turn dependent from the experimentally observed number of events \( N_{\alpha\alpha} \). To obtain a realistic estimation of \( \kappa \) the Bayes’ theorem needs to be introduced. Using Equation (S12) in the Bayes’ theorem, the probability density function of the deposition rate \( \kappa \) under the condition that \( N_{\alpha\alpha} \) events were actually observed, can be given as:

\[
p(\kappa | N_{\alpha\alpha}) = \frac{P_{\text{events}}(N_{\alpha\alpha} | \kappa) \cdot p(\kappa)}{\int_{0}^{\infty} P_{\text{events}}(N_{\alpha\alpha} | \kappa) \cdot p(\kappa) \, d\kappa}
\]  

(S14)
Here, \( p(κ) \) is the \textit{a priori} probability distribution of the deposition rate. Since \textit{no a priori} knowledge about this quantity is available, a constant non-informative pseudo-prior was used. Thus, Equation (S14) can be analytically evaluated to be:

\[
p(κ|N_{a-ads}) = D \cdot \frac{(κ)^{N_{a-ads}}}{N_{a-ads}!} \cdot e^{-κD}
\]

Equation (S15) represents a skew distribution function. The formal similarity of Equations (S11) and (S15) is a mathematical particularity in the case of Poisson distributions.

It is assumed that the most probable value of \( κ \), i.e., the maximum value (mode point) of \( p(κ|N_{ads}) \), is the one realized during the experiment for a certain \( T_{ads} \). This value is denominated \( κ_{mp} \). In order to obtain the error limits on the calculated \( κ_{mp} \). Bayes credible intervals need to be calculated. Integration of \( p(κ|N_{ads}) \) allows for transforming the probability density function \( p(κ|N_{ads}) \) into the probability \( P(κ|N_{ads}) \) function. The probability that the deposition rate \( κ \) is smaller than the limiting parameter \( K \) is:

\[
P(K|N_{a-ads}) = \int_0^K p(κ|N_{a-ads}) \cdot dκ = 1 - Q(N_{a-ads}; K)
\]

The function \( Q(N_{a-ads}; K) \) in Equation (S16) represents the regularized incomplete Euler gamma function (Euler integral of the second kind). The latter is defined as:

\[
Q(x; x) = \int_x^\infty \frac{z^{x-1} e^{-z}}{\Gamma(x)} \cdot dt
\]

with \( \Gamma(x) \) being the ordinary gamma function and \( Q(z; 0) = 1 \) for any value of \( z \).

Due to the skewness of the distribution function, the asymmetric lower \( (κ_{low}) \) and upper \( (κ_{up}) \) boundaries of the credible interval (i.e., the probability that the parameter is within the interval) to the envisaged coverage level \( θ \) (i.e., the probability that the credible interval covers with a probability \( θ \) the true value) are obtained by solving the following equations:

\[
Q(N_{a-ads}; κ_{low}) = 1 - (1 - θ) \cdot \left(1 - Q(N_{a-ads}; κ_{mp})\right)
\]

\[
Q(N_{a-ads}; κ_{up}) = 1 - (1 - θ) \cdot Q(N_{a-ads}; κ_{mp})
\]

4. Deduction of the \( ΔH_{ads}(DBOCl_3) \) on quartz

The microscopic migration of a molecule down the chromatographic column can be simulated via a Monte-Carlo approach, i.e., by a series of exponentially distributed jumps interposed to a number of adsorption-desorption steps on the chromatographic surface and individual life-times according to decay statistics [6]. While the jumps are responsible for the migration, the adsorption-desorption steps together with the diffusion in the gas phase contribute to the total net retention time. From considerations in [7], the relative probability of an atom of \(^{262}\)Db to travel along the entire length of the chromatography column before its decay – in other words, the \( Y_{igc} \) at a certain \( T_{ads} \) related to the \( Y_{igc} \) at the reference temperature \( T^0 \) – can be deduced to be:

\[
Y_{igc}(l|ΔH_{ads}; T_{ads}) = A \frac{2π}{\sqrt{(l)^2}} \cdot e^{-\frac{(l)^2}{2}} \cdot \left(1 + e^{-\frac{ΔH_{ads}}{RT_{ads}}}\right)^{-1}
\]

with

\( l \) – length of the chromatographic column;

\( T^0 \) – reference temperature (0 °C);

\( R \) – universal gas constant.

The value of the constant parameters \( A \), \( B \), and \( C \) were obtained as follows. First of all, a series of Monte-Carlo simulations was performed using values of \( ΔH_{ads} \) in the range \(-165 \text{ kJ mol}^{-1} < ΔH_{ads} < -115 \text{ kJ mol}^{-1} \). This gave a set of hypothetical external chromatogram. The uncertainty on the yields of each chromatogram was considered Poisson distributed. By using Equation (S20), individual fits of the external chromatograms allowed for obtaining the parameters \( A \), \( B \), and \( C \) as:
A = 0.986 ± 0.020
B = 6.831 ± 0.016
C = 1.1992 × 10^{11} ± 9.6 × 10^8

These parameters simultaneously reproduce all the hypothetical external chromatograms well. Keeping these parameters constant, the adsorption enthalpy $\Delta H_{ads}$ was fitted using Equations (S13) and (S20):

$$\kappa_\infty = (97.6 ± 26.4) \text{ atoms C}^{-1}$$

$$\Delta H_{ads} = (-130 ± 6) \text{ kJ mol}^{-1}$$

The experimental and estimated chemical yields together with 68% confidence interval limits are shown in Table S3. These are depicted in the external chromatogram shown in the manuscript.

| $T_{iso}$ (°C) | Beam dose (10^{-6} °C) | $Y_{exp,\text{low}}$ (%) | $Y_{exp}$ (%) | $Y_{exp,\text{up}}$ (%) | $Y_{igc,\text{low}}$ (%) | $Y_{igc}$ (%) | $Y_{igc,\text{up}}$ (%) |
|---------------|------------------------|------------------------|--------------|------------------------|------------------------|--------------|------------------------|
| 600           | 26206805               | 33                     | 51           | 86                     | 72                     | 98           | 134                    |
| 550           | 22646491               | 82                     | 119          | 182                    | 72                     | 98           | 133                    |
| 450           | 25274603               | 33                     | 54           | 98                     | 68                     | 90           | 120                    |
| 400           | 29268767               | 39                     | 61           | 103                    | 51                     | 64           | 80                     |
| 375           | 64138376               | 29                     | 42           | 64                     | 25                     | 36           | 52                     |
| 350           | 44856808               | 0                      | 0            | 11                     | 4                      | 10           | 23                     |

5. Extrapolation of the sublimation enthalpy of Db, $\Delta H_{sub}(Db)$

Correlations between the standard formation enthalpies of the solid state, $\Delta H_s$, versus the corresponding values of the gaseous state, $\Delta H_g$, have been successfully applied in [8-10]. For group-5 oxychlorides (MOCl$_3$), the empirical correlation between $\Delta H_s$ (MOCl$_3$) and $\Delta H_g$ (MOCl$_3$) gives the linear relation:

$$\Delta H_f, g(MOCl_3) = -\left[2.28 \cdot \Delta H_f, g(MOCl_3) + 836.5\right], \text{ kJ mol}^{-1} \quad (S21)$$

Equation (S21) was obtained with thermochemical data from [11]. Commonly, the first elements of each group of the Periodic Table show significant differences in the chemical behavior in comparison to the rest of the group, i.e., their heavier homologues; the standard state of vanadium oxychloride, VOCl$_3$, is even liquid, and hence, this compound was not included in this analysis. The sublimation enthalpy $\Delta H_{sub}$ corresponds to the difference between $\Delta H_g$ and $\Delta H_s$. Therefore, Equation (S21) can be rewritten as:

$$\Delta H_f, g(MOCl_3) = -\frac{\Delta H_{sub}(MOCl_3) + 836.5}{1.28}, \text{ kJ mol}^{-1} \quad (S22)$$

From the $\Delta H_{sub}(DbOCl_3) = 172 ± 10 \text{ kJ mol}^{-1}$ deduced in this work (see Main Text), the $\Delta H_g(DbOCl_3) = -788 ± 8 \text{ kJ mol}^{-1}$ value is obtained.

Along a group of the Periodic Table, the standard formation enthalpy of monoatomic gaseous elements can be related to the standard formation enthalpy of its compounds in the gas phase [8]. Thus, the standard formation enthalpy of monoatomic gaseous group-5 elements, $\Delta H_g(M)$, based on $\Delta H_g$ (MOCl$_3$), can be expressed as:

$$\Delta H_f, g(M) = -\frac{\Delta H_f, g(MOCl_3) + 273.30}{0.65}, \text{ kJ mol}^{-1} \quad (S23)$$
with M = Nb and Ta. Introducing the \( \Delta H_f (\text{DbOCl}_3) \) value deduced in this work into Equation (S23), \( \Delta H_f (\text{Db}) = \Delta H_{\text{subl}} (\text{Db}) \) is estimated as 792 ± 12 kJ mol\(^{-1}\), making Db one of the least volatile elements of the Periodic Table.

6. References

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Author Contributions

Nadine M. Chiera – Investigation, Conceptualization, Data curation, Formal analysis, Project administration, Supervision, Writing - original draft

Tetsuya K. Sato – Investigation, Conceptualization, Funding acquisition, Project administration, Supervision, Writing - review & editing

Robert Eichler – Formal analysis, Writing - review & editing

Tomohiro Tomitsuka – Investigation

Masato Asai – Investigation

Sadahiro Adachi – Investigation

Rugard Dressler – Formal analysis, Writing - review & editing

Keitaro Hirose – Investigation

Hiroki Inoue – Investigation

Yuta Ito – Investigation, Writing - review & editing

Ayuna Kashihara – Investigation

Hiroyuki Makii – Investigation

Katsuhisa Nishio – Investigation

Minoru Sakama – Investigation

Kozi Shirai – Investigation

Hayato Suzuki – Investigation

Katsuyuki Tokoi – Investigation

Kazukai Tsukada – Investigation

Eisuke Watanabe – Investigation

Yuichiro Nagame – Conceptualization, Supervision, Validation, Writing - review & editing