

Isokinetic behaviour in gas phase catalytic haloarene hydrodehalogenation reactions: Mechanistic considerations

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Abstract

Compensation behaviour is established for the gas phase hydrodehalogenation of a range of haloarenes over a common Ni/SiO₂ catalyst. Analysis of the experimental results delivers an isokinetic temperature (T_{iso}) at 658 ± 2 K associated with the following reactants: chlorobenzene, 4-chlorotoluene, 3-chlorophenol, 1,3-dichlorobenzene, 4-chlorophenol, 3,5-dichlorophenol, 1,4-dichlorobenzene, bromobenzene, 2,6-dichlorophenol, 2-chlorophenol, 1,2-dichlorobenzene and 1,3-dibromobenzene. The occurrence of a T_{iso} is accounted for using the Selective Energy Transfer (SET) model that is based on the premise of resonance between a vibrational mode of the catalyst and a vibrational mode of the reactant with a transferral of resonance energy from the catalyst to the reactant to generate the “activated complex” with subsequent reaction. In this study of a single catalyst promoting a common (hydrodehalogenation) reaction for a family of haloarene reactants, we establish the complimentary vibrational modes as the out-plane C–H vibrations of substituted benzene and Ni–H vibration at high hydrogen surface coverage. The proposed surface rate-determining step is the C–H “out-of-plane” activation favouring an sp^2 to sp^3 transformation.
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1. Introduction

In a recent paper [1] dealing with catalytic hydrodehalogenation over Ni/SiO₂, it was reported that, for a series of haloarene reactants, the kinetic data adhered to what is known as a “compensation effect”, i.e. a linear relation between $\ln A$ (the experimentally determined Arrhenius pre-exponential factor) and E_{exp} (the experimental activation energy). A value of $T_{\text{iso}} = 633$ K, the isokinetic temperature, was extracted from the resultant compensation plot. The “compensation” notation has been introduced to reconcile the seemingly paradoxical situation where an increase in activation energy is accompanied by an increase in the pre-exponential factor [2–4]. While the precise source of compensation behaviour has yet to be conclusively established, plausible explanations that have been advanced invoke active site energy distributions and/or enthalpy/entropy relationships [2] or vibrational activation [4]. Compensation

phenomena in heterogenous catalysis arise in experimental measurements involving a series of related reactions or catalysts and is often associated with structure sensitive reactions. The latter is of significance in this instance as catalytic hydrodehalogenation exhibits significant structure sensitivity [5–10]. A general consensus is emerging [2,4] that the compensation effect arises in the case of experimental measurements where apparent rather than the true Arrhenius parameters (energetics of the surface reaction(s)) are measured. A distinction should be drawn between compensation behaviour and the isokinetic relation. The latter arises where the Arrhenius plots ($\ln k$ versus $1/T$) for a series of very similar reactions intersect at a common temperature. Isokinetic and compensation relationships are by no means synonymous and the establishment of a compensation effect does not necessarily mean that an isokinetic relationship is operative. While the compensation effect can be regarded as an empirical relationship, isokinetic behaviour may be reconciled on the basis of chemical theory [4,11,12]. In the earlier publication [1], catalytic hydrodehalogenation was presented as an innovative methodology for transforming toxic hazardous material into recyclable products. The measurement of T_{iso} is of

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practical value as it may represent a possible working temperature at which to hydrotreat haloarene mixtures. In this report, we have extended the earlier study to include additional catalytic hydrodehalogenation data and have undertaken a rigorous analysis of the significance of the experimentally determined isokinetic temperature.

2. Experimental measurements

The Ni/SiO₂ catalyst was prepared by impregnation of a Cab-O-Sil 5M silica (surface area = 194 m² g⁻¹) with an aqueous solution of Ni(NO₃)₂. The Ni content (4.6%, w/w) was measured by ICP-OES (Vista-PRO, Varian Inc., accurate to within ±2%). BET surface areas, temperature programmed reduction (TPR) and H₂ chemisorption were determined using the commercial CHEM-BET 3000 (Quantachrome) unit, as described in some detail elsewhere [12]. TPR analysis revealed a sharp H₂ consumption peak at ca. 640 K with a secondary peak (at ca. 670 K) and a gradual return to baseline, a reduction pattern that is in good agreement with previous reports of Ni/SiO₂ TPR [13,14] and can be attributed to the decomposition of nickel nitrate to NiO with a subsequent reduction of NiO to Ni⁰ [12]. The BET area (178 m² g⁻¹) and H₂ uptake (0.8 cm³ g⁻¹) measurements (for the post-TPR sample) were reproducible to within ±5%. Prior to catalysis, the catalyst precursor sample, sieved in the 75–150 μm mesh range, was accordingly activated in a 100 cm³ min⁻¹ stream of dry H₂ (99.9%) at a temperature ramp (10 K min⁻¹, controlled using a Eurotherm 91e temperature programmer) to a final temperature of 723 K. The temperature was maintained for 18 h where the catalyst bed temperature was independently monitored using an on-line data logging system (Pico Technology, model TC-08) and found to be constant to within ±1 K. The XRD profile (recorded on an Philips X'Pert instrument using nickel filtered Cu Kα radiation) is characterized by three peaks at 44.5°, 51.8° and 76.3°, corresponding to (1 1 1), (2 0 0) and (2 2 0) planes of metallic nickel that are consistent with an exclusive cubic symmetry. A secondary ion mass spectrometric analysis (SIMS, VG ESCALAB) of the activated catalyst (pressed into indium foil) revealed only the presence of Si, O and Ni on the surface. High-resolution transmission electron microscopy (HRTEM) analysis was carried out using a Philips CM20 TEM microscope operated at an accelerating voltage of 200 kV; metal particle size detection limit = 0.1–0.2 nm. The mean Ni particle diameter based on a measurement of 660 individual particles = 11 nm.

The hydrodehalogenation reactions were conducted with a co-current flow of the haloarene feed in H₂ under atmospheric pressure in a fixed-bed continuous flow glass reactor over the temperature range 423 ≤ *T* ≤ 593 K. Isothermal operation was maintained by diluting the catalyst bed with ground glass (75–150 μm). Interparticle and intraparticle heat transport effects can be disregarded when applying established criteria [15]; the temperature differential between the catalyst particle and bulk fluid phase was <1 K. Plug-flow conditions applied with reactor diameter/catalyst particle ratio = 90. Mass transport contributions under reaction conditions were evaluated taking the approach outlined previously [16] where the molec-

ular diffusion coefficients were calculated using Satterfield's [17] method. The catalytic system was found to operate with negligible diffusion retardation of the reaction rate; effectiveness factor (η) > 0.99 at 573 K. The catalyst was supported on a glass frit and a layer of glass beads above the catalyst bed served as a heating zone, ensuring that the reactants reached the reaction temperature before contacting the catalyst. A Model 100 (kd Scientific) microprocessor controlled infusion pump was used to deliver the halogenated feed via a glass/PTFE airtight syringe and PTFE line at a fixed (calibrated) rate. The ultra pure (99.999%) H₂ was supplied via a Brooks mass flow controller and the flow rate was monitored using a Humonics (Model 520) digital flowmeter. All the halogenated reactants were supplied by Sigma-Aldrich (98–99.9%) and used without further purification. The halogenated feedstock was either fed undiluted to the reactor or diluted in *n*-hexane or methanol where the catalyst weight (*W*) to inlet molar haloarene flow rate (*F_X*) ratio spanned the range 0.4–2762 g h mol⁻¹; methanol and hexane served solely as diluent and did not impact on hydrodehalogenation activity. The H₂ partial pressure was in the range 0.89–0.99 atm where H₂ was at least 10 times in excess relative to stoichiometric quantities. From a consideration of gas phase reaction equilibrium constants [18,19], dehalogenation under the stated reaction conditions can be taken to be irreversible. Adherence to pseudo-first-order kinetics was demonstrated in the earlier study [1]. The specific rate constants extracted from a pseudo-first-order treatment are given in Table 1, wherein the range of halogenated feedstock that was studied is identified. In a series of blank tests, passage of each halogenated feed in a stream of H₂ through the empty reactor, i.e. in the absence of catalyst, did not result in any detectable conversion. Product analysis by capillary GC has been described in some detail elsewhere [12]; the detection limit corresponded to a feedstock conversion <0.1 mol%. A halogen (in the form of HX product) mass balance was performed by passing the effluent gas through an aqueous NaOH (3.5–8.0 × 10⁻³ mol dm⁻³, kept under constant agitation at ≥300 rpm) trap and monitoring continuously the pH change by means of a Hanna HI Programmable Printing pH Bench-Meter. The concentration of hydrogen halide generated was also measured by titrimetric analysis of the NaOH trap solution using a Metrohm (Model 728) Autotitrator (AgNO₃, combined Ag electrode); halogen mass balance was complete to better than ±10%. All the data presented here have been generated in the absence of any significant catalyst deactivation where each catalytic run was repeated (up to six times) using different samples from the same batch of catalyst: the measured rates did not deviate by more than ±8%.

3. Results and discussion

3.1. Analysis of experimental data

Hydrodehalogenation proceeded over Ni/SiO₂ with 100% selectivity to yield a partially or the fully dehalogenated aromatic and HX; there was no evidence of halogen gas formation, aromatic ring reduction or scission of the non-halogen ring substituents. In Fig. 1, we provide a graphical representation of the

Table 1
Collation of the experimental kinetic data

Reactant	$10^3/T$ (K ⁻¹)	$\ln k_{\text{exp}}$ (mol h ⁻¹ g ⁻¹)	E_{exp} (kJ mol ⁻¹)	$\ln A_{\text{exp}}$
Chlorobenzene	1.686	-3.252	59	8.71
	1.745	-3.669		
	1.808	-4.069		
	1.859	-4.145		
	1.912	-4.876		
	2.008	-5.460		
Bromobenzene	1.686	-4.685	92	14.06
	1.745	-5.321		
	1.808	-5.819		
	1.859	-6.599		
	1.912	-7.310		
	2.008	-8.370		
4-Chlorotoluene	1.686	-2.872	49	7.13
	1.745	-3.192		
	1.808	-3.452		
	1.859	-3.693		
	1.912	-4.111		
	2.008	-5.345		
3-Chlorophenol	1.686	-2.603	40	5.35
	1.745	-2.978		
	1.808	-3.305		
	1.859	-3.520		
	1.912	-3.755		
	2.008	-4.130		
2,6-Dichlorophenol	1.686	-3.912	58	7.94
	1.745	-4.418		
	1.808	-4.719		
	1.859	-5.017		
	1.912	-5.395		
	2.008	-6.326		
2,4,5-Trichlorophenol	1.686	-2.580	136	24.91
	1.745	-3.713		
	1.808	-4.630		
	1.859	-5.198		
	1.912	-6.215		
	2.008	-7.830		
Pentachlorophenol	1.686	-4.878	151	25.70
	1.745	-6.195		
	1.808	-7.278		
	1.859	-8.240		
	1.912	-9.321		
	2.008	-10.941		
1,2-Bromochlorobenzene	1.686	-6.022	121	18.27
	1.745	-7.216		
	1.808	-8.035		
	1.859	-8.569		
	1.912	-9.480		
	2.008	-10.712		
1,3-Dichlorobenzene	1.686	-4.025	96	15.58
	1.745	-4.701		
	1.808	-5.269		

Table 1 (Continued)

Reactant	$10^3/T$ (K ⁻¹)	$\ln k_{\text{exp}}$ (mol h ⁻¹ g ⁻¹)	E_{exp} (kJ mol ⁻¹)	$\ln A_{\text{exp}}$
	1.859	-6.156		
	1.912	-6.400		
	2.008	-7.870		
	2.114	-8.925		
1,2,4-Trichlorobenzene	1.686	-4.311	144	24.84
	1.745	-5.542		
	1.808	-6.564		
	1.859	-7.488		
	1.912	-8.569		
	2.008	-10.157		
2-Chlorophenol	1.686	-3.272	38	4.45
	1.745	-3.474		
	1.808	-3.872		
	1.842	-4.023		
	1.912	-4.354		
	2.008	-4.683		
4-Chlorophenol	1.686	-2.930	47	6.60
	1.745	-3.202		
	1.808	-3.640		
	1.832	-3.894		
	1.912	-4.318		
	1.988	-4.694		
3,5-Dichlorophenol	1.686	-3.432	70	10.68
	1.745	-3.987		
	1.808	-4.423		
	1.842	-4.890		
	1.912	-5.402		
	1.988	-6.031		
1,2-Dichlorobenzene	1.686	-4.430	91	14.00
	1.745	-5.169		
	1.808	-5.765		
	1.842	-6.276		
	1.912	-6.931		
	1.988	-7.856		
1,4-Dichlorobenzene	1.686	-3.923	103	16.86
	1.745	-4.804		
	1.808	-5.633		
	1.842	-6.112		
	1.912	-6.813		
	1.988	-7.932		
1,3-Dibromobenzene	1.686	-5.022	131	21.40
	1.745	-6.156		
	1.808	-7.002		
	1.842	-7.744		
	1.912	-8.562		
	1.988	-9.999		
	2.114	-11.802		

experimental data given in Table 1. In the preliminary treatment of a smaller database, a $T_{\text{iso}} = 633$ K was determined [1]. Taking an overview of the extended database plotted in Fig. 1, it appears that some but not all the lines coalesce near this temper-

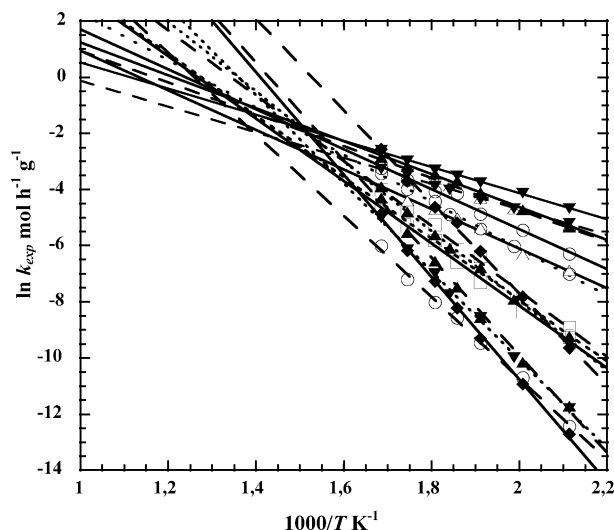


Fig. 1. Plots of the Arrhenius relation for all the investigated systems: (○, full-drawn line) chlorobenzene; (□, full line) bromobenzene; (▲, full line) 4-chlorotoluene; (▼, full line) 3-chlorophenol; (△, full line) 2,6-dichlorophenol; (◆, full line) pentachlorophenol; (◇, broken line) 2,4,5-trichlorophenol; (○, broken line) 1,2-bromochlorobenzene; (□, broken line) 1,3,-dichlorobenzene; (▲, broken line) 1,2,4-trichlorobenzene; (▼, broken line) 2-chlorophenol; (△, broken line) 4-chlorophenol; (○, dotted line) 3,5-dichlorophenol; (□, dotted line) 1,2-dichlorobenzene; (▲, dotted line) 1,4-dichlorobenzene; (▼, dotted line) 1,3-dibromobenzene.

ature. By trial and error, we can identify three groups of data, two of which present clear cut examples of an isokinetic relationship, as illustrated in Figs. 2 (Group I) and 3 (Group II). The remaining four reactants (in Group III) exhibit Arrhenius lines with roughly equal activation energies, running more or less parallel to each other (Fig. 4). It should be noted that Group III includes polysubstituted haloarenes (with fewer C–H bonds), an important consideration as shall be seen when explaining isokinetic behaviour on a mechanistic level. It should also be

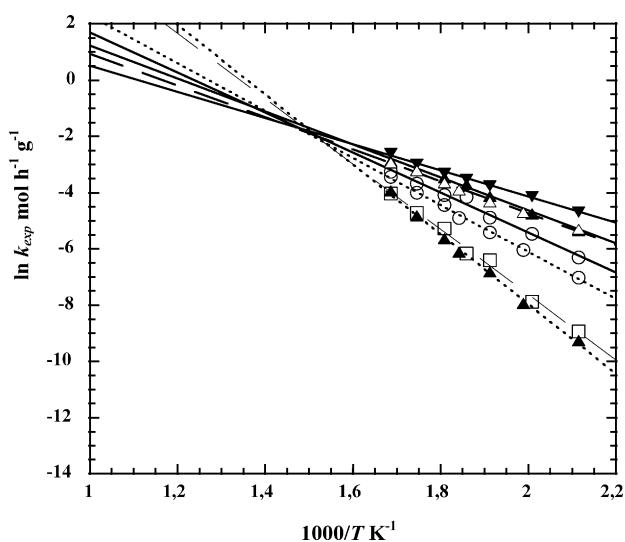


Fig. 2. Plots of the Arrhenius relations associated with the Group I reaction system: (○, full line) chlorobenzene; (▲, full line) 4-chlorotoluene; (▼, full line) 3-chlorophenol; (□, broken line) 1,3,-dichlorobenzene; (△, broken line) 4-chlorophenol; (○, dotted line) 3,5-dichlorophenol; (▲, dotted line) 1,4-dichlorobenzene.

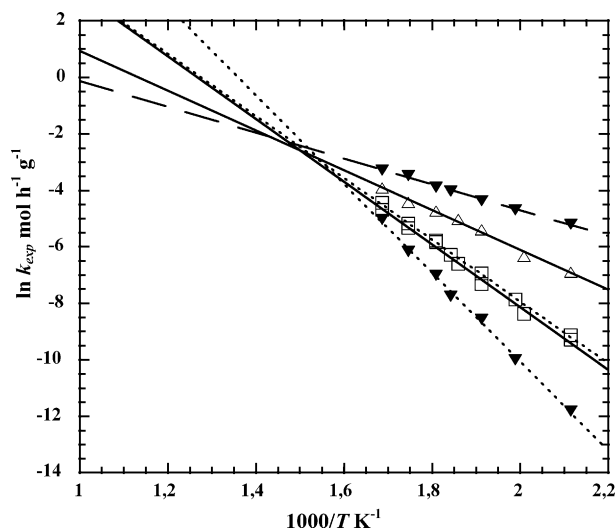


Fig. 3. Plots of the Arrhenius relations associated with the Group II reaction system: (□, full line) bromobenzene; (△, full line) 2,6-dichlorophenol; (▼, broken line) 2-chlorophenol; (□, dotted line) 1,2-dichlorobenzene; (▼, dotted line) 1,3-dibromobenzene.

noted that the dehalogenation of 1,2-bromochlorobenzene (a member of Group III) involves a combined hydrodebromination and hydrochlorination (Cl exchange) as composite reaction steps and so the mechanism is quite distinct from that associated with the other haloarenes as is outlined elsewhere [12,20]. Taking the data plotted in Figs. 2 and 3, one can extract a value of $1000/T_{\text{iso}} = 1.5 \pm 0.2$ for both systems with a corresponding $\ln k_{\text{iso}} = -1.75$ associated with Group I and $\ln k_{\text{iso}} \approx -2.5$ for Group II. The difference in reaction rate, i.e. $\Delta \ln k_{\text{iso}} \approx 0.75$, suggests that the reactivity of haloarenes in Group I is twice that of the members of Group II. This may be explained on the basis of steric effects where the Group II chloroarene reactants possess an *ortho*-substituted Cl while Group I di-substituted benzenes only bear *meta*- and *para*-positioned Cl. It has been established elsewhere [1,18,19] that steric hindrance due to close proximity

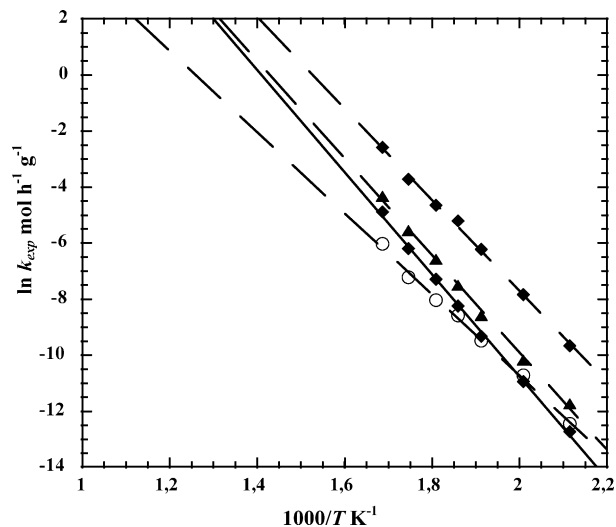


Fig. 4. Plots of the Arrhenius relations associated with the Group III reaction system: (◇, broken line) 2,4,5-trichlorophenol; (◆, full line) pentachlorophenol; (○, broken line) 1,2-bromochlorobenzene; (▲, broken line) 1,2,4-trichlorobenzene.

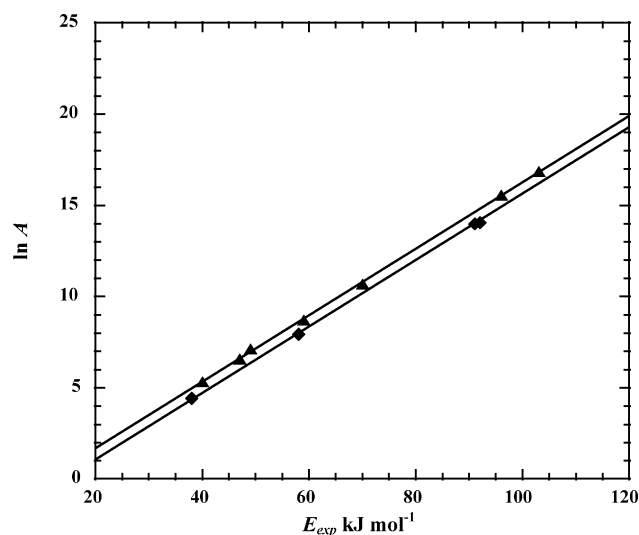


Fig. 5. A “compensation plot” for the Group I (\blacktriangle , $y = -1.9518 + 0.18227x$, $R^2 = 0.99959$) and Group II (\blacklozenge , $y = -2.5819 + 0.18234x$, $R^2 = 0.99976$) reaction systems; see Figs. 2 and 3 for reactants in both Groups.

of substituents on the ring impedes the rate of hydrodehalogenation. Moreover, the lower reactivity associated with Group II bromobenzene and 1,3-dibromobenzene can be attributed to inductive effects where a lower electron density at the aromatic ring carbon(s) (in the presence of Br relative to Cl) serves to inhibit hydrodehalogenation [1,12,20], as is addressed in our discussion of reaction mechanism below. The combined T_{iso} for Groups I and II is 667 ± 80 K, which is in reasonable agreement with the earlier report [1]. Treating both groups separately to generate individual compensation plots, the results are shown in Fig. 5 which yields T_{iso} values of 656 and 660 K for Groups I and II, respectively; correlation coefficients for both fits are close to 1 (see figure caption). We accordingly adopt a $T_{\text{iso}} = 658 \pm 2$ K from this point onwards as a basis for model development and reaction mechanism analysis. This initial screening of experimental results has delivered 12 hydrodehalogenation datasets with a common Ni/SiO₂ catalyst that exhibit both conventional compensation behaviour, while also possessing a clear isokinetic component.

3.2. The SET model

From the outset, it is tempting to attempt to apply the model of vibrational resonance to these data. This model has been developed and tested in several reaction systems by one of us [21]. The main idea is that there prevails a state of resonance between a vibrational mode (ω) of the catalyst system and that vibrational mode of the reacting molecule (ν), which is most likely to carry the reactant towards the shape and form of the “activated complex”. This activation requires a transferral of resonance energy from the catalyst system to the reactant and when the reactant has received a suitable number of vibrational quanta, reaction proceeds. Such is the premise on which the Selective Energy Transfer (SET) model is based. The following relation has been

deduced between T_{iso} , ω and ν [21].

$$T_{\text{iso}} = Nhc R^{-1} (\nu^2 - \omega^2) \omega^{-1} \times \{\pm\pi/2 - \arctg[0.5\nu\omega(\nu^2 - \omega^2)]^{-1}\}^{-1} \quad (1)$$

where N represents the Avogadro number, c the velocity of light, h the Planck constant and R is the gas constant. Where $\omega = \nu$, in which case one has maximum efficiency of resonance energy transfer, it holds [21] that

$$T_{\text{iso}} = \frac{Nhc}{2R\nu} = 0.719\nu \quad (2)$$

These relations have been tested and verified in a number of cases, e.g. the catalytic oxidation of propene and toluene [22], the catalytic hydrogenolysis of neopentane [23], a homogeneous non-catalytic (ligand substitution) reaction [24], the reaction of carbon dioxide at metal surfaces [25] and the hydrogenolysis of ethane [26]. A further confirmation of the (pragmatic) value of the SET approach has recently been presented [27]. In treating the gas phase, non-catalytic reaction between carbon dioxide and free lanthanide atoms, the kinetics of which had been described by Campbell [28], it was demonstrated [27] that the isokinetic relation found for some of the lanthanide elements was described not by Eq. (2) that relates to condensed systems, but by the corresponding relation

$$T_{\text{iso}} = \frac{Nhc}{R\nu} \quad (3)$$

This relation had originally been derived [21] for systems where only one route of energy dissipation was assumed to be at hand, i.e. a gas phase reaction. This finding serves to illustrate the wide ranging applicability of the SET model.

3.3. Application of the SET model to catalytic hydrodehalogenation

As a first approximative approach one can assume that a full resonance occurs, without specifying the nature of the catalyst vibrational mode. Using the value for T_{iso} reported above (658 ± 2 K), one can calculate the value of the reactant vibrational mode:

$$\nu = \frac{658}{0.719} = 915 \text{ cm}^{-1}$$

This value (915 cm^{-1}) falls within the range of out-of-plane C–H vibrations of substituted benzene, which differ depending on the type and pattern of substitution [29]. The out-of-plane C–H vibrations for the compounds in Groups I and II, taken from Varsanyi’s compilation [29], are given in Table 2. In terms of the SET model, we must match our value of $\nu = 915 \text{ cm}^{-1}$ with a complimentary vibrational mode in this catalyst system that supports resonance at this wave number. As the reactions were promoted using a Ni/SiO₂ catalyst, an obvious choice of vibrational mode is that corresponding to a Ni–H vibration. The review by Mate et al. [30] provides a number of choices for these vibrations: $\omega = 1100$ and 940 cm^{-1} for high hydrogen coverage and 1080 cm^{-1} for low coverage on Raney nickel; $\omega = 1060$ and

Table 2

C–H out-of-plane vibration frequencies for Groups I and II reactants, taken from Varsanyi's compilation [29] where they are denoted as "molecular vibration 17b"

Reactant	Group	ν "17b" (cm^{-1})
Chlorobenzene	I	902
4-Chlorotoluene	I	806
3-Chlorophenol	I	887
1,3-Dichlorobenzene	I	867
4-Chlorophenol	I	822
3,5-Dichlorophenol	I	909
1,4-Dichlorobenzene	I	815
Bromobenzene	II	904
2,6-Dichlorophenol	II	^a
2-Chlorophenol	II	937
1,2-Dichlorobenzene	II	815
1,3-Dibromobenzene	II	869

^a The value for 2,6-dichlorophenol is not included in Ref. [29].

940 cm^{-1} for low and high hydrogen coverage, respectively, on Ni(1 1 0). High hydrogen coverage should apply in our reaction system where the hydrogen supply is maintained far in excess of reaction stoichiometry. Moreover, there is evidence [31] in the literature supporting non-competitive adsorption of hydrogen and haloarene during hydrodehalogenation over Ni/SiO₂. However, all the above values for ω fall outside the range of values for substituted arene out-of-plane vibrations and we cannot simply apply Eq. (2) but we have to fall back on the more general Eq. (1). Taking the value $\omega = 940 \text{ cm}^{-1}$ (or 950 cm^{-1}), i.e. high hydrogen coverage, Eq. (1) delivers a T_{iso} dependence on ν that is valid for a series of similar (but not identical) molecules where ν varies within narrow limits. The resultant curves are shown in Fig. 6 wherein it can be seen that T_{iso} is largely invariant ($655 \pm 10 \text{ K}$) over the ν range $770\text{--}910 \text{ cm}^{-1}$. The T_{iso} value that results from an application of the SET model is strikingly similar to the value that we arrived at ($658 \pm 2 \text{ K}$) from an analysis of the experimental data. On the other hand, had we used

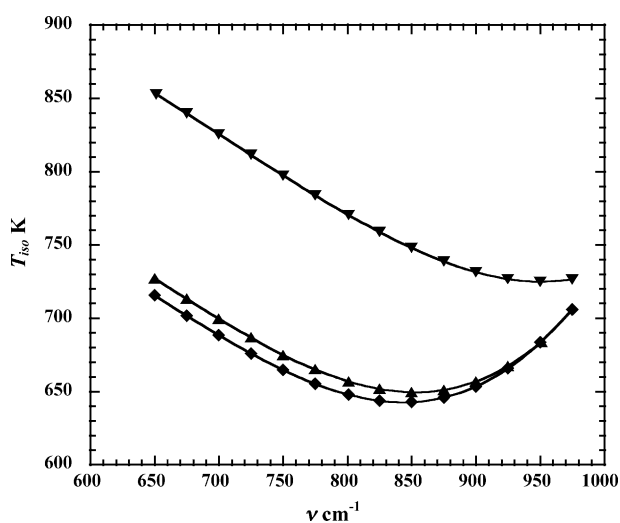


Fig. 6. Calculated (from Eq. (1)) T_{iso} as a function of the frequency of the vibration of the reacting molecule (ν) for a set of assumed values of the heat bath frequencies: 940 cm^{-1} (\blacklozenge), 950 cm^{-1} (\blacktriangle) and 1060 cm^{-1} (\blacktriangledown).

the low coverage value for Ni–H vibrations, i.e. 1060 cm^{-1} , the resulting curve (see Fig. 6) does not yield any value of T_{iso} which approaches that found experimentally. Perhaps one should comment at this stage on the difference between our treatment and the strategy that has been typically applied in those studies that have made use of Eq. (1). In the latter cases, an isokinetic relationship was reached by slight variations within a family of catalysts, i.e. varying ω , used to promote a common reaction, whereas in the present case the isokinetic relationship is the result of slight variation in reactants, i.e. varying ν , where the catalyst is fixed. It is worth flagging the work of Wootsch and Paál [32,33] who established isokinetic and compensation behaviour for a range of *n*-hexane skeletal reactions in the presence of H₂ over supported Pt. There is, however, no presumption made in the deduction of Eq. (1) with regard to the manner with which the activation energy is varied; the only demand is that it does actually vary. We can therefore apply freely Eq. (1) to the case under consideration.

3.4. Suggested mechanism

Taking an overview of the existing literature dealing with gas phase heterogeneously catalyzed haloarene hydrodehalogenation, some consensus of opinion [31,34,35] is now emerging that supports a surface mechanism involving dissociative adsorption of the haloarene with the formation of a surface σ -complex via the aromatic ring carbon with the highest electron density. A dissociative haloarene adsorption finds support in published halogen atom exchange studies [35,36]. One can visualize a mechanism involving a surface interaction where the arene molecule is 'co-planar' with the metal surface. The various substituents can cause a certain tilt with respect to the surface and the slow step is then a transformation of an sp^2 carbon towards an sp^3 state of hybridization. As indicated by the SET analysis, the out-of-plane motion of the C–H groups makes room for interaction with surface metal atoms. One can envisage the variation in activation energy as caused by the larger or smaller tilt of the flat molecule, creating a facile or more difficult approach to the metal atom in the rate limiting step. The thus formed sp^3 centre will cause the entire arene structure to change, making the C–X bond more or less susceptible to hydrogen attack (from Ni–H), releasing the X substituent to form HX as product with Ni–C (sp^3) bond decomposition to yield the arene product. One must note, that the Ni–H "units" serve the purpose of donating (resonance) energy to activate the C–H out-of-plane vibration and are also active reactants.

3.5. Activation energies

It follows [21] from the deduction of Eq. (1) that the activation energy should be considered, in terms of the proposed model, as the sum of a series of vibrational quanta. Indeed, this has been found to be the case for decomposition reactions involving formic acid [37]. For systems where the anharmonicity constant is small, the difference between two values of activation energies should also be a sum of vibrational quanta. In order

Table 3
Analysis of consecutive differences, ΔE_{exp} , of the experimentally determined activation energies

Reactants	E_{exp} (kJ mol ⁻¹)	ΔE_{exp} (kJ mol ⁻¹)	$n(11)$	$n(10)$	$n(9)$
Chlorobenzene	59				
Bromobenzene	92	33	3	3	4
4-Chlorotoluene	49	43	4	4	5
3-Chlorophenol	40	9	1	1	1
2,6-Dichlorophenol	58	18	2	2	2
1,3-Dibromobenzene	131	73	7	7	8
1,3-Dichlorobenzene	96	35	3	4	4
2-Chlorophenol	38	58	5	6	6
4-Chlorophenol	47	9	1	1	1
3,5-Dichlorophenol	70	23	2	2	2
1,2-Dichlorobenzene	91	21	2	2	2
1,4-Dichlorobenzene	103	12	1	1	1
		44	4	4	5
Ordinate ($x=0$, kJ mol ⁻¹)			-0.46	0.28	1.40
Slope (kJ mol ⁻¹)			11.0	10.1	8.8

Note: only those systems are included that yield an isokinetic relationship.

to test this in the present case, we have used the experimentally determined activation energies (E_{exp}) reported in Table 1; the results of the analysis for the 12 “isokinetic” haloarenes is presented in Table 3. By trial and error one can estimate the least common factor (F) of the series of E_{exp} differences (ΔE_{exp}) and from this, one can calculate the vibrational frequency that should correspond to this entity. The choice of the best possible value for F is based on a plot of ΔE_{exp} against the appropriate quantum number (n). In Fig. 7, we demonstrate such a procedure for the assumption that the least common factor is 9 kJ mol⁻¹; the abscissa ($n(9)$) denotes the number with which 9 is contained in any difference value (the ordinate, ΔE_{exp}). The resultant slope (8.8 kJ mol⁻¹) provides an improved value over the initial “guess”, i.e. 9 kJ mol⁻¹. However, the line does

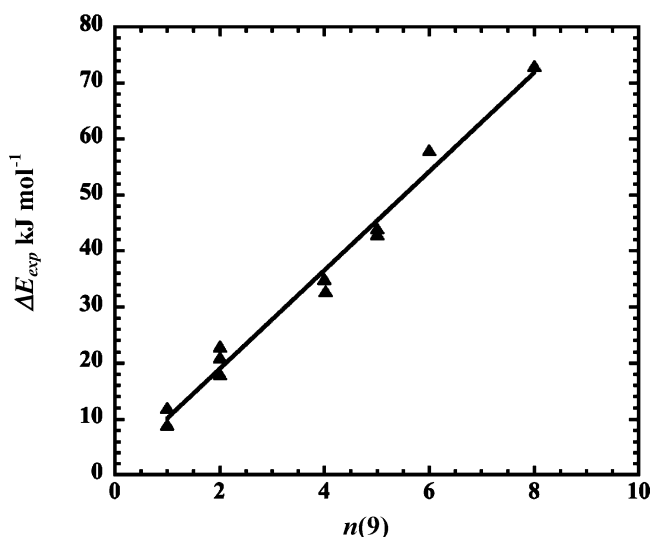


Fig. 7. Example of the relationship between the differential values of the experimentally determined activation energy (E_{exp}) reported in Table 2 and a number (n) that should best describe the differences as a multiple of a “first guess” value, in this case 9 kJ mol⁻¹, i.e. $n(9)$. The line is described by: $y = 1.3953 + 8.8111x$, $R^2 = 0.98524$.

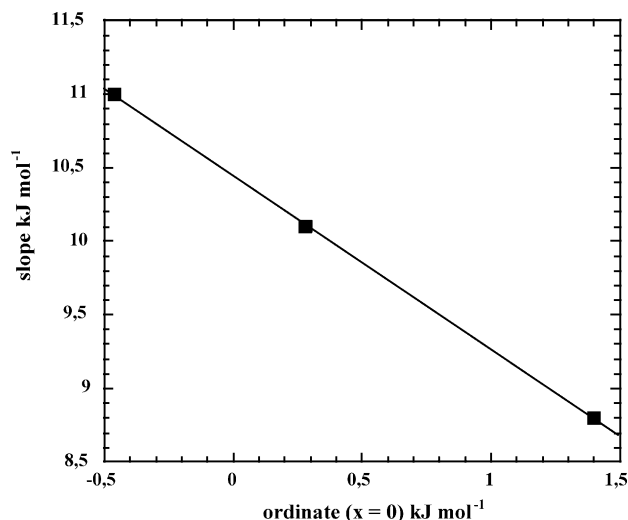


Fig. 8. Graphical treatment of the results from Fig. 7 and two analogous plots with the additional common factors 10 ($n(10)$) and 11 ($n(11)$) kJ mol⁻¹. The value for the “slope” is plotted against the intercept of the ordinate in Fig. 7. This yields the proportionality factor $n (=10.4)$ where $\Delta E_{\text{exp}} = nF$.

not pass through the *origin*, which should be the case if a strict proportionality, i.e. $\Delta E_{\text{exp}} = nF$, was operating. Extending the analysis further, the results arising from two additional F values (10 and 11 kJ mol⁻¹) are included in Table 3. As these lines, also, did not pass through the origin, we have plotted the associated slopes against the ordinate values at $n=0$ in Fig. 8 and extracted by interpolation the value of the “slope” that should result where the abscissa and the ordinate are both zero. Such a value is found to be 10.4 kJ mol⁻¹, corresponding to (ν) 872 cm⁻¹. This value is in good agreement with the range of vibrational frequencies of the out-of-plane vibrations of substituted benzenes and is close to the minimum exhibited by the T_{iso} versus ν curves shown in Fig. 6 where $\omega = 950/940$ cm⁻¹. It must be stressed that this analysis also holds for the assumption of a term in the activation energy representing heat of adsorption, as long as this term is constant for all the systems under investigation. Of course, any such system with a constant term added to or subtracted from the real activation energy, will give the same slope in a compensation plot and consequently, the same value of T_{iso} .

4. Conclusions

Gas phase hydrodehalogenation of a range of mono-, di- and tri-haloarenes over Ni/SiO₂ where $423 \leq T \leq 593$ K yields the partially dehalogenated or fully dehalogenated parent aromatic as the sole products. Catalysis was operated in the absence of any significant mass or heat transfer limitations with a catalyst weight to inlet molar haloarene flow rate in the range 0.4–2762 g h mol⁻¹, H₂ partial pressure (0.89–0.99 atm) such that H₂ was at least 10 times in excess relative to stoichiometric quantities with an overall raw rate measurement reproducibility better than $\pm 8\%$. Applying pseudo-first-order kinetics for plug-flow operation delivered 16 k_{exp}/T datasets, analysis of which has allowed us to identify a group of 12 haloarene reactants that exhibit compensation behaviour with an associated $T_{\text{iso}} = 658 \pm 2$ K. The

remaining four reactants, polysubstituted haloarenes with fewer C–H bonds, exhibit (more or less parallel) Arrhenius lines and (roughly equal) activation energies. In terms of the SET model we propose that the existence of this T_{iso} can be linked to a critical reactant vibrational mode, out-of-plane C–H vibration, that matches with a complimentary catalyst vibrational mode, Ni–H vibration, which supports optimum resonance energy transfer. We have demonstrated that $\omega = 950/940 \text{ cm}^{-1}$ (catalyst driving vibrational mode, corresponding to Ni–H surface vibration) yields a $T_{\text{iso}} = 655 \pm 10 \text{ K}$ if the energy accepting vibration, ν , is in the range $840 \pm 70 \text{ cm}^{-1}$. This latter frequency range covers out-of-plane vibrations from virtually all substituted arene molecules. Furthermore, such frequencies are consistent with the set of experimentally determined activation energies. Our data treatment is consistent with a surface mechanism involving haloarene/catalyst interaction where the arene molecule is co-planar with the surface, the slow step is an activation of the out-of-plane C–H bond(s), i.e. transformation of sp^2 carbon to hybridised sp^3 followed by a fast hydrogenolytic attack at a C–X bond by hydrogen dissociated at the Ni sites.

References

- [1] M.A. Keane, Appl. Catal. A: Gen. 271 (2004) 109.
- [2] G.C. Bond, M.A. Keane, H. Kral, J.A. Lercher, Catal. Rev. Sci. Eng. 42 (2000) 323.
- [3] A.K. Galwey, Adv. Catal. 26 (1977) 247.
- [4] L. Liu, Q.-X. Guo, Chem. Rev. 101 (2001) 673.
- [5] S.B. Halligudi, B.M. Devassay, A. Ghosh, V. Ravikumar, J. Mol. Catal. A: Chem. 184 (2002) 175.
- [6] W. Juszczuk, A. Malinowski, Z. Karpinski, Appl. Catal. A: Gen. 166 (1998) 311.
- [7] A.R. Suzdorf, S.V. Morozov, N.N. Anshits, S.I. Tsiganova, A.G. Anshits, Catal. Lett. 29 (1994) 49.
- [8] G. Pina, C. Louis, M.A. Keane, Phys. Chem. Chem. Phys. 5 (2003) 1924.
- [9] M.A. Keane, C. Park, C. Menini, Catal. Lett. 88 (2003) 89.
- [10] L.N. Zanaevskii, V.A. Aver'yanov, Yu.A. Treger, Russ. Chem. Rev. 65 (1996) 617.
- [11] W. Linert, R.F. Jameson, Chem. Soc. Rev. 18 (1989) 477.
- [12] K.V. Murthy, P.M. Patterson, M.A. Keane, J. Mol. Catal. A: Chem. 225 (2005) 149.
- [13] J. Zielinski, Catal. Lett. 31 (1995) 47.
- [14] M.A. Keane, Can. J. Chem. 72 (1994) 372.
- [15] J.R. Welty, C.E. Wicks, R.E. Wilson, Fundamentals of Momentum, Heat and Mass Transfer, John Wiley, New York, 1984.
- [16] G. Tavoularis, M.A. Keane, J. Chem. Technol. Biotechnol. 74 (1999) 60.
- [17] D.N. Satterfield, Heat Transfer in Heterogeneous Catalysis, M.I.T. Press, Cambridge, MA, 1970.
- [18] E.-J. Shin, M.A. Keane, Chem. Eng. Sci. 54 (1999) 1109.
- [19] E.-J. Shin, M.A. Keane, J. Chem. Technol. Biotechnol. 75 (2000) 159.
- [20] C. Park, C. Menini, J.L. Valverde, M.A. Keane, J. Catal. 211 (2002) 451.
- [21] R. Larsson, J. Mol. Catal. 55 (1989) 70.
- [22] R. Larsson, Chem. Scr. 27 (1987) 371.
- [23] Z. Karpinski, R. Larsson, J. Catal. 168 (1997) 532.
- [24] R. Larsson, Inorg. Chim. Acta 191 (1992) 179.
- [25] R. Larsson, J. Mascetti, Catal. Lett. 48 (1997) 183.
- [26] D. Lomot, W. Juszczuk, Z. Karpinski, R. Larsson, J. Mol. Catal. A: Chem. 186 (2002) 163.
- [27] R. Larsson, J. Mascetti, React. Kinet. Catal. Lett. 85 (2005) 107.
- [28] M.L. Campbell, Phys. Chem. Chem. Phys. 1 (1999) 3731.
- [29] G. Varsanyi, Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives, Adam Hilger, London, 1974.
- [30] C.M. Mate, B.E. Bent, G.A. Somorjai, in: Z. Paal, P.G. Menon (Eds.), Hydrogen Effects in Catalysis, Marcel Dekker Inc., New York, 1988 (Chapter 2).
- [31] M.A. Keane, D.Yu. Murzin, Chem. Eng. Sci. 56 (2001) 3185.
- [32] A. Wootsch, Z. Paál, J. Catal. 185 (1999) 192.
- [33] A. Wootsch, Z. Paál, J. Catal. 205 (2002) 86.
- [34] B.F. Hagh, D.T. Allen, Chem. Eng. Sci. 45 (1990) 2695.
- [35] Yu.A. Serguchev, Yu.V. Belokopytov, Kinet. Catal. 42 (2001) 174.
- [36] Kiyonari, Y. Kensci, Nippon Kagaku Kaishi 12 (1989) 1999.
- [37] Larsson, M.H. Jamroz, M.A. Borowiak, J. Mol. Catal. A: Chem. 129 (1998) 41.